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Main-Group Chemistry

Interpnictogen Cations: Exploring New Vistas in Coordination Chemistry

*Alasdair P. M. Robertson, Paul A. Gray, and Neil Burford**

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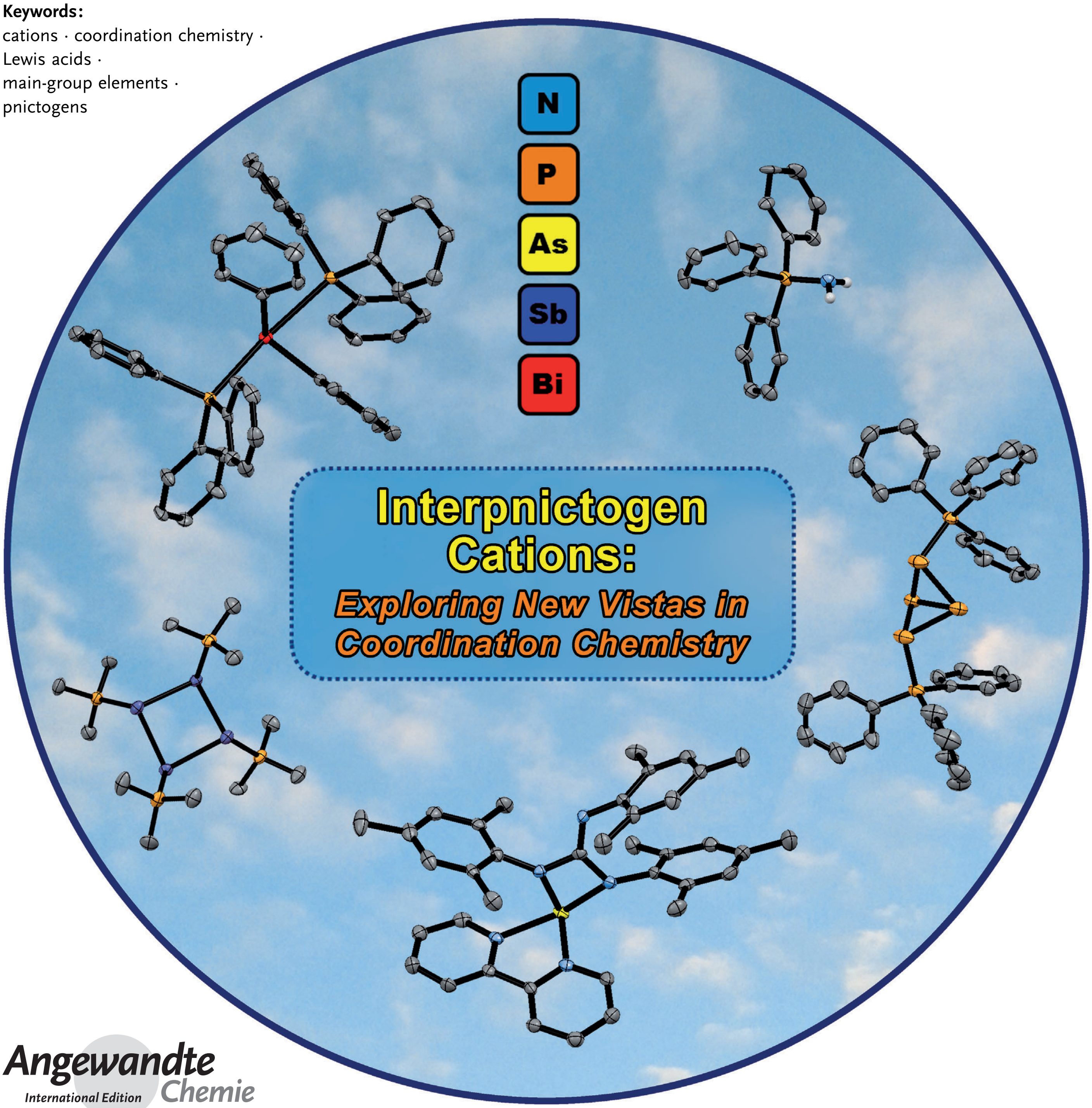

Pnictine derivatives can behave as both 2e$^-$ donors (Lewis bases) and 2e$^-$ acceptors (Lewis acids). As prototypical ligands in the coordination chemistry of transition metals, amines and phosphines also form complexes with p-block Lewis acids, including a variety of pnictogen-centered acceptors. The inherent Lewis acidity of pnictogen centers can be enhanced by the introduction of a cationic charge, and this feature has been exploited in recent years in the development of compounds resulting from coordinate Pn–Pn and Pn–Pn′ interactions. These compounds offer the unusual opportunity for homoatomic coordinate bonding and the development of complexes that possess a lone pair of electrons at the acceptor center. This Review presents new directions in the systematic extension of coordination chemistry from the transition series into the p-block.

From the Contents

1. Introduction

Amines and phosphines represent prototypical ligands in the broad array of established coordination chemistry of d- and f-block metals and many p-block elements. Moreover, any Group 15 element (the pnictogens, Pn = N, P, As, Sb, Bi) in a neutral trivalent framework (e.g. PnX_3, PnR_3) has the potential to act as a 2e$^-$ donor (Lewis base), although the donor strength is generally greater for elements with smaller atomic radii. Consequently, complexes involving heavier pnictines as ligands are rare compared to those involving amines or phosphines.

The pnictogen elements also have the ability to behave as Lewis acceptor centers (Lewis acids) and extensive coordination chemistry has been established for compounds of antimony and bismuth.[1–3] In contrast, the relatively low Lewis acidity and small covalent radii of nitrogen, phosphorus, and arsenic generally limit their behavior as acceptors. The introduction of a cationic charge by abstraction of an anionic substituent, however, enhances the Lewis acidity of the pnictogen center and creates a vacant coordination site suitable for donor ligation. Formation of new Pn−Pn′ bonds by this process, which is effective for all the pnictogen elements, offers a versatile method for the synthesis of cationic interpnictogen compounds and complexes of acceptor centers that bear a lone pair of electrons. As important main-group analogues of transition-metal coordination complexes, these pnictogen-centered complexes may find applications in catalysis, small-molecule activation, or as materials precursors.

1.1. Scope and Concepts of Structure, Bonding, and Synthesis

As a consequence of the continuing, and sometimes artificial, demarcation of the chemical sciences, parallels between the reactivity of chemical subgroups are often overlooked. This is particularly true of coordination chemistry, which is indelibly linked to the transition metals, but can be considered to have significant generality across the periodic table. This concept was elegantly described by Lehn in his Nobel Prize lecture of 1987:[4] “*the chemistry of artificial receptor molecules may be considered a generalized coordination chemistry, not limited to transition metal ions but extending to all types of substrates (receptees): cationic, anionic, or neutral species of organic, inorganic or biological nature.*”

This Review highlights the application of Pn–Pn coordination chemistry in the formation of interpnictogen cations, demonstrating the efficacy of this method for all of the pnictogen elements. Cationic compounds containing Pn−P bonding (for Pn = N, P) have previously been reviewed,[5–10] therefore, discussion of these compounds emphasizes recent developments. To appreciate the hybrid nature of the bonding in these compounds, foundational concepts and definitions regarding structure and bonding are discussed in Section 2, together with an overview of synthetic methods. The abbreviations for compound names and parameters applied throughout the document are defined in Ref. [11].

2. Terms and Geometric Parameters

The terms valence, coordination number, oxidation state, VSEPR[12] geometry, and molecular geometry are important descriptors of structure and bonding. However, some of these terms have been applied with a degree of ambiguity that has prompted recent insightful clarification.[13–15] We have defined

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[*] Dr. A. P. M. Robertson, B.Sc. P. A. Gray, Prof. N. Burford
Department of Chemistry, University of Victoria
Victoria, BC V8W 3V6 (Canada)
E-mail: nburford@uvic.ca

our use of the terms below as applied to interpnictogen cations:

Valence: the number of pairs of bonding electrons at a featured atomic center.

Coordination number: the number of atoms directly bonded to a featured atomic center.

Oxidation state: the charge remaining on an atom following the heterolytic removal of all substituents, when the electrons associated with a bond remain with the more electronegative atom. Electrons associated with a coordinatively bound ligand are removed with the ligand, irrespective of the relative electronegativities of the donor/acceptor.

Geometry: the polyhedron formed by the substituents and/or ligands around a featured atomic center.

Stereochemically active lone pair: a lone pair of electrons at a featured center, the presence of which has a measurable effect on the structural orientation of substituents around the center, often modeled effectively by VSEPR theory.

Coordination complex: an assembly consisting of a central atom (usually metallic) to which is attached a surrounding array of other groups of atoms (ligands).[16] Coordinate bonds are primarily defined as those which undergo heterolytic bond cleavage as the minimum-energy bond-rupture process,[17] and in reciprocal, are formed heterolytically by a $2e^-$ donor–acceptor interaction.

Ligand: An ion or molecule that can have an independent existence,[18] and can interact with an acceptor center through the donation of a nonbonding electron pair.

Where available and pertinent, graphical views of representative solid-state structures, prepared using ORTEP-V V2.02, are presented with thermal ellipsoids at the 50% probability level. Unless they are responsible for an important structural feature, all anions and hydrogen atoms are omitted for clarity, with labeling limited to feature atoms. Where discernible contacts between anion(s) and cation(s) prevail, we classify a compound as ionic when the solid-state structure exhibits interionic distances that are at least 1 Å longer than the sum of the covalent radii between the atomic centers (Σ_{CR})—a value which may be less than the sum of the van der Waals radii. Feature Pn–Pn or Pn′–Pn bond lengths are discussed to illustrate the magnitude of the interaction and are compared with Σ_{CR} for the two elements (listed in Table 1) under discussion. The Σ_{CR} values listed are calculated from the mean single-bond covalent radii of the various elements provided in the two most recent reports,[19,20] which present similar values for covalent radii determined from different methods.

Table 1: Estimates of the sums of covalent radii (Σ_{CR} [Å]) for combinations of pnictogen elements.

	N	P	As	Sb	Bi
N	1.42	–	–	–	–
P	1.80	2.18	–	–	–
As	1.91	2.29	2.40	–	–
Sb	2.11	2.49	2.60	2.80	–
Bi	2.21	2.59	2.70	2.90	3.00

2.1. Lewis Acceptor Pnictogen Centers

A variety of in situ generated (see Section 2.3) pnictogen-centered cations can be envisaged as potential Lewis acceptor units, and are notionally limited to three classes that are correlated with the perceived oxidation state (+I, +III, or +V) at the pnictogen acceptor (Figure 1). Many interpnictogen cations derive from the acceptor class **2A** (pnictenium), although examples of complexes involving acceptors of classes **1A**, **2B**, **2C**, and **3B** have also been reported, and are subsequently described.

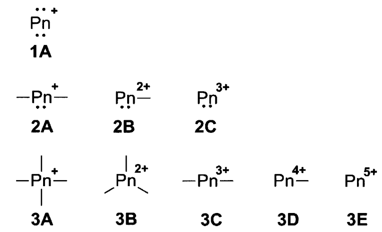


Figure 1. Positively charged pnictogen centers as potential Lewis acceptors.

Alasdair P. M. Robertson graduated in chemistry at the University of St Andrews, Scotland, in 2008 with an MChem, 1st Class Honours, with a final year research project in the group of Prof. Derek Woollins. He subsequently completed a PhD at the University of Bristol in 2012 under the supervision of Prof. Ian Manners, focusing on the metal-catalyzed/thermolytic dehydrogenation of amine-borane adducts. Since then, he has been working as a postdoctoral research fellow with Prof. Burford at the University of Victoria.

Paul A. Gray completed his BSc Honours in 2012 at Acadia University in Wolfville, Nova Scotia (Canada). His final year research project on the utility of phosphorus-centered cations in synthesis was completed under the supervision of Prof. Bobby Ellis. He is currently carrying out PhD research with Prof. Burford at the University of Victoria, where he is working on developing the coordination chemistry of the p-block elements. He holds an NSERC Alexander Graham Bell Canada Graduate Scholarship and a President's Scholarship.

2.2. Interpnictogen Bond Character

Interpnictogen cations have been described using two distinct bonding notations. For the prototypical cations $[R_3Pn'{-}PnR_2]^+$, a coordinate notation invokes a pnictine ligand on a pnictenium (**2A**) acceptor (Figure 2a, case 1), with the Pn−Pn bond represented by an arrow, that is, donor→acceptor. Alternatively, the Lewis model involves a pnictino substituent bound to a tetravalent pnictonium center (Figure 2a, case 3). The dichotomy in nomenclature and bonding notation also applies for complexes of acceptor classes **2B** and **2C** (Figure 2b,c). For consistency, all compounds described in this Review are presented schematically using the "hybrid" notation (Figure 2, case 2).

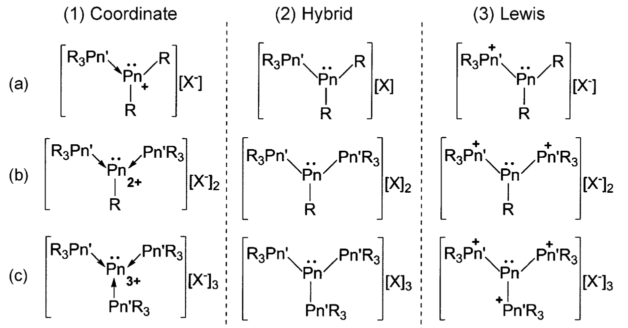


Figure 2. Coordinate, hybrid, and Lewis notations for the bonding in a) $[R_3Pn'{-}PnR_2][X]$, b) $[(R_3Pn')_2PnR][X]_2$, and c) $[(R_3Pn')_3Pn][X]_3$.

Computational studies of the charge distribution have shed light on the bonding in some interpnictogen cations,[21–24] and within these studies, complexes calculated to have high positive charge at the "donor" sites are presented using the Lewis notation.[25] Ligand-exchange reactions are experimentally observed for some interpnictogen salts, implicating heterolytic bond cleavage/formation (see Section 2.3), and suggesting coordinate character in these Pn−Pn bonds. A computational study of prototypical pnictenium acceptors with amine and phosphine ligands concludes that the character of the Pn−Pn bond in derivatives of $[R_3Pn{-}PnR'_2][X]$ is influenced by the substitution at the pnictenium center.[26] We perceive that the character of the Pn−Pn bond varies significantly depending on the elements involved, with the coordinate character greater for the heavier, more metallic elements. It is generally understood that coordinate bonds are significantly longer than Σ_{CR}, and weaker than covalent bonds for which homolytic cleavage is of lower energy than heterolytic cleavage.[17] However, definitive conclusions based on bond-length data alone are precluded by other contributing factors, including coordination number and oxidation state.

Neil Burford obtained a BSc Honours from the University of Wales, Cardiff, and a PhD from the University of Calgary (Canada). Following postdoctoral studies at the University of Alberta and at the University of New Brunswick, he was appointed Assistant Professor at Dalhousie University in 1987, Harry Shirreff Professor of Chemical Research in 2000, and Canada Research Chair Tier I in 2001. He was appointed Chair of the Department of Chemistry at Dalhousie University in 2008, and in 2011 he moved to the University of Victoria as Professor and Chair of the Department of Chemistry.

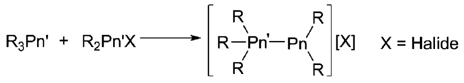
Through consideration of these various factors where available, we infer particular characteristics for the Pn−Pn bonds in the presented interpnictogen cations. However, in our opinion, definitive differentiation between the notations presented in Figure 2 is generally unnecessary, as these notations represent purely conceptual bonding scenarios in which the positive charge is localized at a single atomic center.

2.3. Synthetic Methods

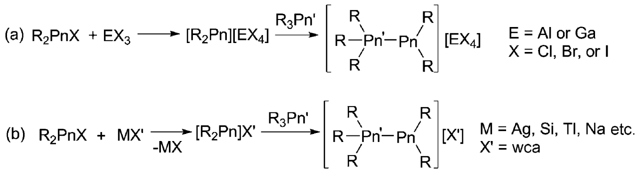
The synthesis of most interpnictogen cations has been achieved through the exploitation of a small number of fundamental methods that invoke Pn–Pn coordinate interactions, and are summarized in Schemes 1, 2, and 3 for complexes of pnictenium (class **2A**) acceptors.

The displacement (or exchange) of a halide substituent from a halopnictine by a neutral pnictine represents a versatile approach to Pn−Pn bond formation. Recently likened to the Menschutkin S_N2 reaction of amines with alkyl halides to yield ammonium salts,[27] the reaction of a chlorophosphine with a trialkylphosphine, for example, yields a P−P-bonded cationic complex $[R_3P{-}PR_2]^+$ with a chloride anion,[28] as illustrated generically for Pn′−Pn bond formation in Scheme 1.

In cases where the neutral halopnictine has insufficient Lewis acidity to engage a ligand, abstraction of the halide with either Group 13 halides (EX_3, E = Al or Ga, X = Cl, Br, or I; Scheme 2a) or by a metathesis reaction with a salt of a weakly coordinating anion (OTf^-, PF_6^-, BF_4^-, ClO_4^-, etc.) or ROTf (R = Me or Me_3Si; Scheme 2b),[8,9] produces a pseudo-pnictenium cation with consequential enhanced Lewis acidity. The



Scheme 1. Halide displacement from a halopnictine by a pnictine to form $[R_3Pn'{-}PnR_2][X]$ salts.



Scheme 2. Generic reactions to form $[R_3Pn'{-}PnR_2][X]$ salts by halide abstraction by a) Group 13 compounds and b) salt metathesis. wca = weakly coordinating anion.

reactions are enthalpically driven by the formation of strong element–halide bonds, gas evolution, or the lattice enthalpies of resulting ionic products. In cases where residual Pn−X (X = Halide) bonds remain, coincident or subsequent redox coupling of pnictogen centers can also lead to the formation of polycationic species.[29–31]

As introduced in Section 2.2, ligand-exchange processes have been demonstrated for some interpnictogen cations,[22,30,32–37] thereby implicating Pn′−Pn coordinate interactions, and providing a versatile route to other interpnictogen cations. These processes are generally driven by the greater Lewis basicity of the incoming ligand (Scheme 3).

$$[R'_3Pn'\text{-}PnR_2][X] \;+\; R''_3Pn'' \;\rightleftharpoons\; [R''_3Pn''\text{-}PnR_2][X] \;+\; R'_3Pn'$$

Scheme 3. Ligand-exchange reactivity of $[R'_3Pn'\text{-}PnR_2][X]$ salts.

3. Cationic Complexes of Nitrogen Acceptors

Although amines and imines are ubiquitous Lewis bases, examples of nitrogen centers behaving as Lewis acceptors are rare, attributed in part to the high Pauling electronegativity and small covalent radius of this element. Nevertheless, compounds of the form $[R_3Pn\text{-}NR_2][X]$ (X = Cl, Br) have been realized through coordination chemistry, although halide displacement/abstraction routes are hampered by the lack of either commercial or synthetically facile sources of haloamines. Nonetheless, the small library of interpnictogen compounds based on notional cationic nitrogen acceptors provides important parallels with heavier analogues.

3.1. Nitrogen Donors on Nitrogen Acceptors

Aminoammonium or hydrazinium salts, $[R_3N\text{-}NR_2][X]$, are accessible by a variety of synthetic routes, most commonly through the reaction of hydrazines, $R_2N\text{-}NR_2$, with alkylating agents or Brønsted acids,[38–42] but contextually through reactions of tertiary amines with a chloroamine (Scheme 4).[36,43]

$$R_3N \;+\; R'_2NCl \;\longrightarrow\; [R_3N\text{-}NR'_2][Cl]$$

Scheme 4. Formation of $[R_3N\text{-}NR'_2][Cl]$ by nucleophilic displacement from NR'_2Cl.

The formation of aminoammonium salts in this manner is postulated to occur by the S_N2 displacement of the chloride anion in "an acid–base reaction in the Lewis sense with chloroamine being the electrophilic reagent",[43] thereby representing a homoatomic coordinate interaction. Moreover, the reaction of $[Me_3N\text{-}NH_2][Cl]$ with Me_3P leads to 20% conversion into $[Me_3P\text{-}NH_2][Cl]$ over 1 week at ambient temperature (Scheme 5),[36] and represents a ligand-exchange process.

Although reactions of tertiary amines with chloroamines cleanly yield aminoammonium salts, nitrogen donors containing acidic hydrogen atoms lead to analogous aminoammonium salts as intermediates, which undergo rapid deprotonation to yield substituted hydrazine derivatives $R_2N\text{-}NH_2$.[43]

$$[Me_3N\text{-}NH_2][Cl] \;+\; PMe_3 \;\xrightleftharpoons[20\ ^\circ C]{1\ \text{week}}\; \underset{20\%}{[Me_3P\text{-}NH_2]Cl} \;+\; \underset{20\%}{Me_3N} \;+\; \underset{80\%}{[Me_3N\text{-}NH_2][Cl]}$$

Scheme 5. Reaction of $[Me_3N\text{-}NH_2]Cl$ with PMe_3.

3.2. Phosphorus Donors on Nitrogen Acceptors

Examples of aminophosphonium cations, $[R_3P\text{-}NR'_2][X]$, have been known since the 1950s and can be accessed by various routes, including salt metathesis and quaternization of aminophosphines.[44–48] They are also, however, formed in the reaction of phosphines with haloamines (Scheme 6),[36,47–53] as exemplified by the reaction of Ph_3P with NH_2Cl in Et_2O solution to quantitatively yield $[Ph_3P\text{-}NH_2][Cl]$. These reactions are again perceived to occur by an S_N2-type reaction of the phosphine donor with an electrophilic nitrogen acceptor. This concept is borne out in the rate of reaction of a trialkylphosphine with a series of haloamines ($NH_2Cl > MeNHCl > Me_2NCl$), which reflects the decreasing Lewis acidity of the chloroamines upon addition of successive methyl groups.[51]

$$R_3P \;+\; R'_2NX \;\longrightarrow\; [R_3P\text{-}NR'_2][X]$$

R = Aryl, Alkyl; R′ = H, Alkyl; X = Cl, Br

Scheme 6. Synthesis of $[R_3P\text{-}NR'_2][X]$ salts by nucleophilic displacement from R'_2NX.

A degree of multiple N−P bonding (see Figure 3) in aminophosphonium cations is evidenced by relatively short N−P bonds (ca. 1.63 Å,[46,54–58] $\Sigma_{CR} = 1.80$ Å) and planarity of the nitrogen center in most examples, which is rationalized by interaction of the lone pair of electrons at the nitrogen atom with σ* orbitals at the phosphorus center.[59,60] The extent of multiple N−P bonding in $[Ph_2(Bn)P\text{-}NEt_2][Cl]$, to our knowledge the only attempt to quantify such an interaction, is estimated to be 30–40%,[55] thereby implicating contributions from both resonance structures in Figure 3.[54,61,62] Further evidence of multiple bonding is suggested by the similar chemical shifts in the ^1H NMR spectra of the methyl protons of $[Me_3P\text{-}NH_2][Cl]$ ($\delta = 1.91$ ppm) and $[Me_4P][I]$ ($\delta = 1.92$ ppm),[49] which may indicate that the σ-electron withdrawal by the nitrogen atom in the cation is countered or cancelled by the π-donation. Consistently, $[Me_2(Ph)P\text{-}NH_2][Cl]$ exhibits a chemical shift of $\delta = 2.19$ ppm in the ^1H NMR spectrum, as a result of the electron-withdrawing effect of the aryl group, which cannot engage in π-bonding.[49]

$$[R'_3P{-}\ddot{N}R_2]^+ \;\longleftrightarrow\; [R'_3P{=}NR_2]^+$$

Figure 3. Resonance structures for $[R_3PNR_2]^+$ cations:

3.3. Arsenic Donors on Nitrogen Acceptors

Analogous to the reactions of both amines and phosphines, reactions of tertiary arsines with chloroamines furnishes aminoarsonium complexes (Scheme 7).[49,63–65] These compounds behave as heavy analogues of aminophosphonium cations and are also speculated to include a degree of π-back-donation of the nitrogen lone pair of electrons.[49] Consistently, the only crystallographically characterized example, [nPr$_3$As-NH$_2$][Cl],[65] reveals a short As–N bond [1.79 Å, $\Sigma_{CR} = 1.91$ Å].

$$R_3As + R'_2NCl \longrightarrow [R_3As{-}NR'_2][Cl]$$

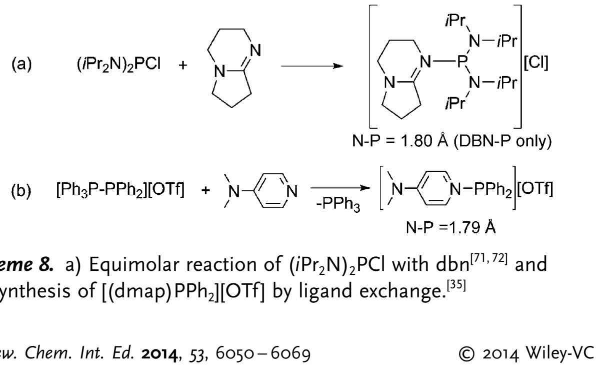
Scheme 7. Synthesis of aminoarsonium salts by reaction of tertiary arsines with haloamines.[49,63–65]

4. Cationic Complexes of Phosphorus Acceptors

Although phosphonium salts, [R$_4$P][X], represent the most extensive series of phosphorus compounds containing a cationic center, examples of complexes which invoke phosphonium centers (class **3A**) as acceptors are rare. By comparison, complexes of phosphenium cations (class **2A**)[8,66] have been established with nitrogen, phosphorus, arsenic, and antimony donors. As stated previously, cationic complexes containing N–P and P–P bonds have been reviewed previously.[5–10] and these sections, therefore, focus primarily upon the most recent contributions.

4.1. Nitrogen Donors on Phosphorus Acceptors

Intramolecular donor–acceptor interactions of pendant amine substituents with the phosphorus centers of halophosphines have been shown in some cases to lead to ionic formulations by effecting halide displacement.[5,67] Corresponding intermolecular interactions have also been reported in reactions of dmap with PX$_3$ (X = Cl or Br), and spectroscopic evidence has been reported for [(dmap)$_2$PCl][X]$_2$, [(dmap)$_3$P][X]$_3$, and [(dmap)$_2$P][X].[68–70] Analogous reactions have also been reported between dbn and aminochlorophosphines, and [(dbn)P(NiPr$_2$)$_2$]$^+$ has been crystallographically characterized as the chloride salt (Scheme 8a).[71,72] The diphenylphosphenium derivative, [(dmap)PPh$_2$][OTf], has also been synthesized by ligand exchange, through the treatment of [Ph$_3$P-PPh$_2$][OTf] with dmap (Scheme 8b).[35]



Scheme 8. a) Equimolar reaction of (iPr$_2$N)$_2$PCl with dbn[71,72] and b) synthesis of [(dmap)PPh$_2$][OTf] by ligand exchange.[35]

A diverse series of amine and pyridine (L) stabilized phosphorus-centered cations is accessible by the displacement of the triflate anion from Mes*NPOTf, with derivatives of [L-PNMes*][OTf] (Figure 4) illustrating complexes of monodentate, bidentate, tridentate and bridging ligands.[35,73,74] In the solid state, the N–P bond lengths are generally longer for complexes with a larger number of donor atoms, in line with the perceived dispersion of the positive charge to the donor sites.

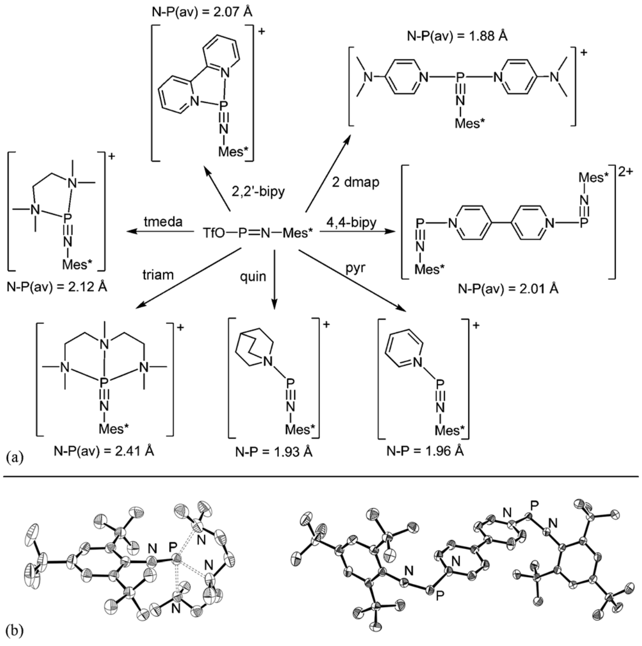


Figure 4. a) Formation of [L-PNMes*]$^+$ by nucleophilic displacement of the triflate anion from Mes*NPOTf. Bond length values are given for N–P single bonds only. b) Representative solid-state structures of the cations in [(triam)PNMes*][OTf] and [Mes*NP(4,4′-bipy)PNMes*]-[OTf]$_2$.[35,73,74]

The cations described above illustrate that interaction of an N-donor is promoted by the formal coordinative unsaturation at the phosphorus acceptor. However, unique examples of complexes of phosphorus acceptors with greater coordination numbers and valencies have also been reported (Figure 5). For example, a neutral 1:1 adduct is observed from the reaction of dmap with (Mes*N)$_2$PX, with excess dmap effecting displacement of the halide to give the salt [(dmap)$_2$P(NMes*)$_2$][X] (Figure 5a).[75] A related complex, [(pyr)$_2$PS$_2$][I], can also be formed from the reaction of [(pyr)P(Cl)S$_2$] with Me$_3$SiI in pyridine (Figure 5b).[76] Similarly, [(dmap)PCl$_2$(NMes*)][X][77] and [(dmap)PMe$_3$]-[OTf]$_2$[32] are formed by single and double halide abstraction from Mes*NPCl$_3$ and Me$_3$PCl$_2$, respectively, in the presence of dmap to form mono- and dicationic phosphorus complexes (Figure 5c,d). Notably, the dication in [(dmap)PMe$_3$][OTf]$_2$ was shown to undergo ligand exchange in the presence of Me$_3$P at ambient temperature to yield the diphosphonium salt [Me$_3$P-PMe$_3$][OTf]$_2$.[32]

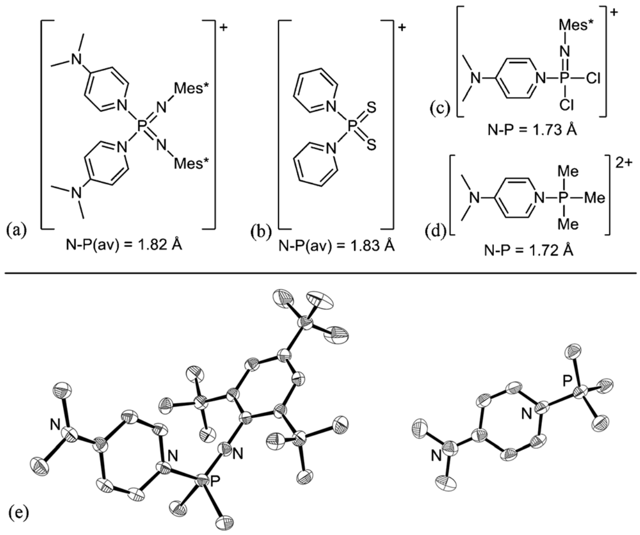


Figure 5. a–d) Examples of cations containing tetracoordinate phosphorus centers involving dmap ligands and e) solid-state structures of the cations in [(dmap)PCl_2(NMes*)][OTf] and [(dmap)PMe_3][OTf]$_2$.[32, 75–77]

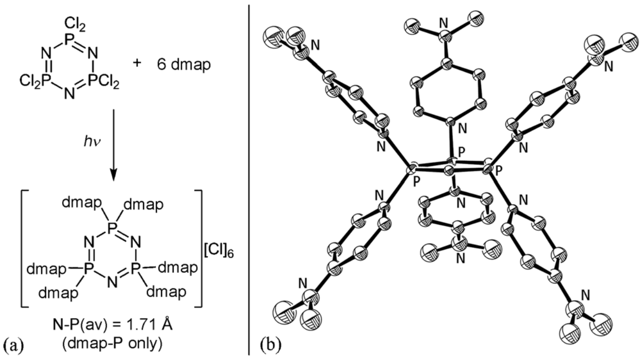
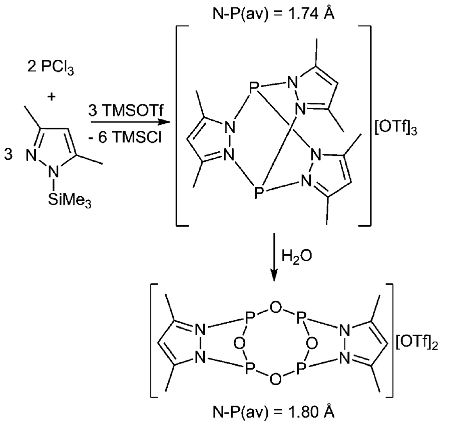


Figure 6. a) Synthesis of [{$(dmap)_2PN$}$_3$][Cl]$_6$ and b) solid-state structure of the hexacation.[78]

A unique example of a hexacation is obtained from treatment of *cyclo*-triphosphazene [N-PCl_2]$_3$ with six equivalents of dmap under microwave irradiation, which effects displacement of all six chloride anions from the phosphorus centers (Figure 6a).[78] The solid-state structure of the salt, formulated as [{$(dmap)_2PN$}$_3$][Cl]$_6$, includes twenty molecules of $CHCl_3$ within the asymmetric unit. In the hexacation, two dmap ligands are bound to each phosphorus center (Figure 6b), with the chloride anions in three distinct sites. The exocyclic N–P bond lengths are relatively short and fall within a narrow range (average: 1.71 Å).

The reaction of TMSpyra with PCl_3 in the presence of TMSOTf furnishes [$(pyra)_3P_2$][OTf]$_3$, which is composed of two phosphorus centers mutually ligated by three pyrazole rings (Scheme 9).[79] Although the phosphorus centers are equivalent, the complex can be viewed as containing an unusual tripyrazole interaction with a P^{3+} acceptor (class **2C**). Hydrolysis of this trication initially gives the dimeric species [(μ-O)$_2${$(pyra)P_2O$}$_2$][OTf]$_2$, and eventually leads to the formation of pyrazolium triflate [pyra][OTf] and P_4O_6.



Scheme 9. Synthesis and hydrolysis of [$(pyra)_3P_2$][OTf]$_3$.[79]

The geometrical parameters for the cationic phosphorus frameworks in the solid state show significant variations, with the N–P bonds resulting from coordinate interactions of N-donors ranging from 2.41 Å in [(triam)PNMes*][OTf] to 1.71 Å in [{$(dmap)_2PN$}$_3$][Cl]$_6$, with many longer than the sum of the covalent radii of the two elements ($\Sigma_{CR} = 1.80$ Å). In general, the N–P bonds are shorter for complexes with a greater cationic charge, consistent with an enhanced Lewis acidity of the acceptor and presumably charge delocalization onto the ligands. Conversely, longer N–P bonds are generally observed for complexes with larger numbers of donors at the phosphorus acceptor center, consistent with dispersion of the positive charge onto the ligands and a greater steric crowding at the acceptor center.

4.2. Phosphorus Donors on Phosphorus Acceptors

Despite the similarities between the chemistry of phosphorus and carbon,[80] the range of known C–C-bonded compounds is vastly greater than that of P–P-bonded compounds, partly because of the higher C–C bond enthalpy (346 kJ mol^{-1}; cf. P–P: 201 kJ mol^{-1})[81] and the limited number of synthetic methods for the formation and manipulation of P–P bonds. However, introduction of a positive charge effects a strengthening of the P–P bond,[8,10,28] which enables the more general development of P–P-bonded compounds, a route not generally applied for carbon.

Cations resulting from the interaction of tertiary phosphines with Lewis acidic phosphorus centers, [R_3P-PR_2][X], were first evidenced by ^{31}P NMR spectroscopy[82–85] and prototypical examples were obtained by halide abstraction from halophosphines[86] or organohalophosphines[34,87–89] in the presence of phosphine ligands, or by nucleophilic halide displacement by phosphine donors (Figure 7a,c).[28] Analogous complexes containing a dicoordinate phosphorus center bound to a tetracoordinate phosphorus center have been reported for a variety of acceptor sites that involve a P=Y bond (Y = CR_2, NR, or PR; Figure 7b).[90–92]

Salts of the form [R_3P-P-PR_3][$AlCl_4$] can be attained by reactions of PCl_3 with phosphines in the presence of $AlCl_3$, and were the subject of a recent review.[7] The resulting

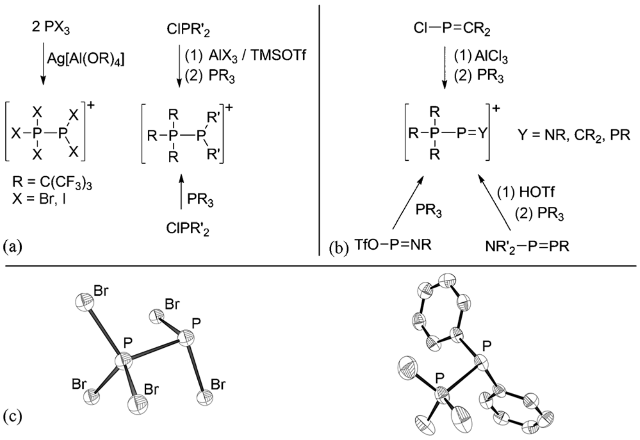
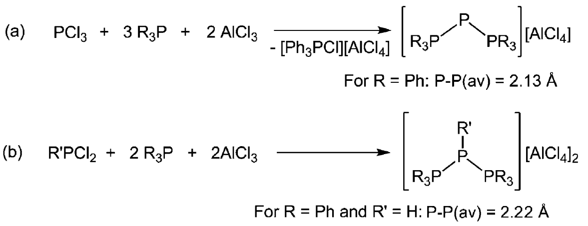


Figure 7. a,b) Synthesis of cations containing P–P bonds by coordination of neutral P donors to phosphorus cations and c) representative solid-state structures of $[Br_3P\text{-}PBr_2]^+$ and $[Me_3P\text{-}PPh_2]^+$.[28,34,86–93]



Scheme 10. a) Redox reaction/abstraction at PCl_3 to form bis(phosphine) complexes of P^+[7,94] and b) formation of $[(R_3P)_2PR'][AlCl_4]_2$ by halide abstraction/donor coordination.[97]

complexes, often termed triphosphenium cations, can be viewed as bis(phosphine) complexes of P^+, a class **1A** acceptor (Scheme 10a).[94] Diphosphine ligands involving organic tethers (e.g. dmpe, dppe) form the analogous cyclic derivatives, for which a series of compounds has been described.[95,96] Under the same conditions, dihalophosphines do not lead to complexes of class **1A** type acceptors, but form symmetric dicationic frameworks composed of two tetracoordinate phosphorus centers bound to a tricoordinate phosphorus center, interpreted to result from the interaction of two phosphine ligands with RP^{2+}, an example of a class **2B** acceptor (Scheme 10b).[97] An array of heterocyclic derivatives of this class of compound have also been obtained by using chelating diphosphine ligands.[6]

In contrast to the outcome presented in Scheme 10b, salts of the form $[R_3P\text{-}P(R')Cl][OTf]$, i.e. containing residual P-Cl functionality, can be obtained by restricting the stoichiometric ratio of phosphine to dichlorophosphine.[29] Subsequent reaction with Ph_3P effects reductive coupling of the P–Cl bonds to give derivatives of $[R_3P\text{-}P(R')(R')P\text{-}PR_3]^{2+}$ and the phosphonium salt $[Ph_3PCl][Cl]$ as the oxidation product (Figure 8). The tetraphosphorus dicationic chain can be considered as a phosphine complex of a bisphosphenium dication acceptor, $[R'P\text{-}PR']^{2+}$.[29,98] An analogous tetraphosphorus dicationic chain is formed in the disproportionation reactions of *peri*-bis(phosphine)-substituted naphthalene frameworks.[88,99]

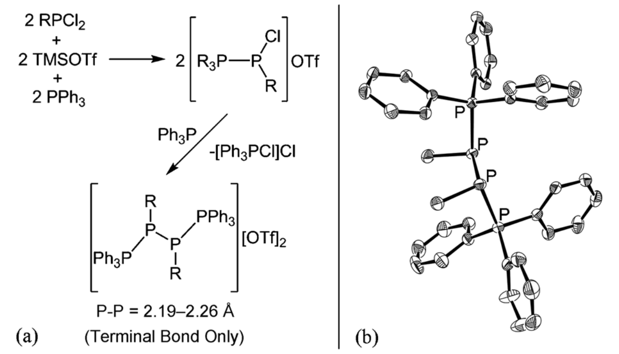
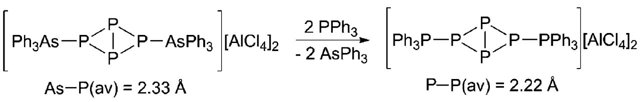


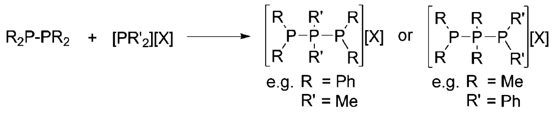
Figure 8. a) Synthesis of $[Ph_3P\text{-}P(R')(R')P\text{-}PR_3][OTf]_2$. b) Solid-state structure of the cation in $[Ph_3P\text{-}P(Me)(Me)P\text{-}PPh_3][OTf]_2$.[29]



Scheme 11. Formation of $[Ph_3P\text{-}P_4\text{-}PPh_3][AlCl_4]_2$ by ligand exchange.[22]

An unusual hexaphosphorus dication has also been obtained through the ligand-exchange reaction of $[Ph_3As\text{-}P_4\text{-}AsPh_3][AlCl_4]_2$ (see Section 4.3) with PPh_3[22] (Scheme 11).

The majority of the polyphosphorus cations described thus far have been attained either by halide abstraction or ligand-exchange methods. An important subclass of compounds, however, which result from insertion reactions of pseudo-phosphenium cations into neutral polyphosphorus frameworks merit brief discussion. This reactivity is illustrated in its simplest form for diphosphines, which react with sources of a phosphenium (R'_2P^+) cation to yield products consistent with a coordination of the phosphenium ion by the diphosphine $[R_2P\text{-}PR_2\text{-}PR'_2]^+$, or products in which the phosphenium inserts into the P–P bond, $[R_2P\text{-}PR'_2\text{-}PR_2]^+$,[100,101] depending on the substitution at the phosphine and diphosphine (Scheme 12). Similar processes are also observed upon reaction of *cyclo*-phosphines[100,102–104] or P_4[86,101,105–107] with phosphenium cations, which lead to P–P insertion and formation of cationic polyphosphorus rings or cages, respectively. The mechanism, although not extensively studied, is postulated to proceed through an initial coordination of the phosphinic donor to the phosphenium center.



Scheme 12. Synthesis of polyphosphorus cations by reaction of diphosphines with in situ generated phosphenium cations.

4.3. Arsenic Donors on Phosphorus Acceptors

In contrast to the array of cations formed through P-P donor–acceptor interactions, analogous reactions with arsenic

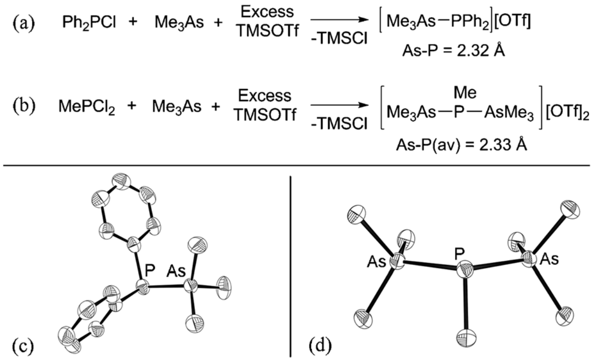


Figure 9. Synthesis of a) $[Me_3As-PPh_2][OTf]$ and b) $[Me_3As-P(Me)-AsMe_3][OTf]_2$. c,d) Solid-state structures of the respective cations.[108]

donors are rare. Reactions of $AsMe_3$ with $ClPR_2$ (R = Me or Ph) in the presence of excess TMSOTf yield salts of the form $[Me_3As-PR_2][OTf]$ through the interaction of $AsMe_3$ with an in situ generated phosphenium center (Figure 9a).[108] Where R = Ph, the structure of the cation (Figure 9c) reveals a relatively long As−P bond (2.3239(6) Å, $\Sigma_{CR} = 2.29$ Å), consistent with those in the corresponding bis(arsine) complexes $[Me_3As-P(Me)-AsMe_3][OTf]_2$, which are formed in the analogous reactions of AsR_3 (R = Me, Ph) with Cl_2PR (R = Me, Ph, Et, Cy, *i*Pr) in the presence of excess TMSOTf (Figure 9b).

Ligand exchange has also enabled the formation of derivatives of $[R'_3As-P(R)(R)P-AsR'_3][X]_2$, which can be interpreted as bis(arsine) complexes of dicationic bis(phosphenium) acceptors $[RP-PR]^{2+}$ (Figure 10a), an analogue of the bis(phosphine) diphosphorus dication $[R_3P-P(R)(R)P-PR_3]^{2+}$ (see Figure 8). Treatment of a solution of $[Ph_3Sb-P(Ph)(Ph)P-SbPh_3][AlCl_4]_2$ with an excess of R_3As (R = Me, Et, or Ph) leads to a quantitative displacement of the stibine donors, driven by the greater Lewis basicity of the arsine.[30] In the solid state, the representative complex $[Me_3As-P(Ph)(Ph)P-AsMe_3][AlCl_4]_2$ (Figure 10b) exhibits statistically identical As−P bond lengths (2.3101(9) Å, $\Sigma_{CR} = 2.29$ Å), which are comparable to those in $[Me_3As-PPh_2][OTf]$ and $[Me_3As-P(Me)-AsMe_3][OTf]_2$.

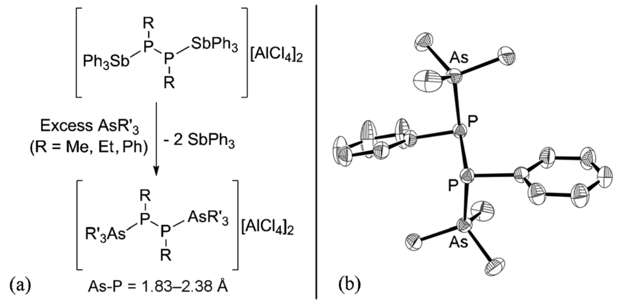


Figure 10. a) Synthesis of $[R_3As-P(Ph)(Ph)P-AsR_3][AlCl_4]_2$. b) Structure of the cation in $[Me_3As-P(Ph)(Ph)P-AsMe_3][AlCl_4]_2$.[30]

A redox reaction is observed for the mixture of PCl_3, $AsPh_3$, and $AlCl_3$ (Figure 11a) to give five equivalents of $[Ph_3As-AsPh_3][AlCl_4]_2$ and $[Ph_3As-P_4-AsPh_3][AlCl_4]_2$, which contains a cluster dication (Figure 11b; see also Scheme 11),[22] with As−P bond lengths in the latter comparable with those in prototypical arsinephosphenium cations. Although a computational study indicated that much of the positive charge in $[Ph_3As-P_4-AsPh_3]^{2+}$ is located on the Ph_3As ligands (+1.88 e), the arsines can be readily exchanged for PPh_3 to furnish $[Ph_3P-P_4-PPh_3][AlCl_4]_2$ (see Section 4.2), in line with the reported description of this complex as a bis(arsine) complex of a P_4^{2+} dication.

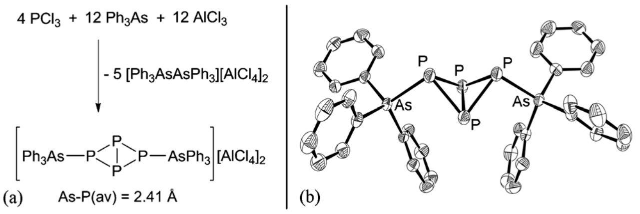


Figure 11. a) Synthesis of $[Ph^3As-P_4-AsPh_3][AlCl_4]_2$. b) Structure of the dication.[22]

4.4. Antimony Donors on Phosphorus Acceptors

Reactions yielding cations containing Sb−P bonds are extremely rare, with the only reported examples resulting from reactions of $SbPh_3$, $AlCl_3$, and $RPCl_2$ (R = Me, Ph, Et, *i*Pr, Cy) to form $[Ph_3Sb-P(R)(R)P-SbPh_3][AlCl_4]_2$, independent of the reaction stoichiometry (Figure 12a).[30] The reactions presumably occur through the interaction of a stibine ligand with an in situ generated chlorophosphenium center, with reductive coupling of the resulting complex leading to the final product and consequential oxidation of Ph_3Sb to form Ph_3SbCl_2. The Sb−P bonds within the two crystallographically characterized cations (R = *i*Pr or Ph) are similar in length (Figure 12b), averaging 2.52 Å ($\Sigma_{CR} = 2.49$ Å).

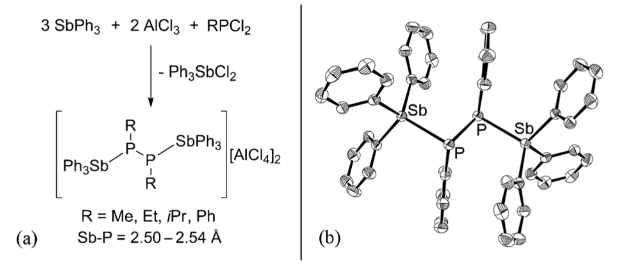


Figure 12. a) Syntheses of $[Ph_3Sb-P(R)(R)P-SbPh_3][AlCl_4]_2$. b) Structure of the cation in $[Ph_3Sb-P(Ph)(Ph)P-SbPh_3][AlCl_4]_2$.[30]

5. Cationic Complexes of Arsenic Acceptors

Complexes of cationic arsenic acceptors have been generated through syntheses invoking N-As, P-As, and As-As donor–acceptor interactions. These complexes provide analogies with complexes of phosphorus, perhaps because of the similar covalent radii (P: 1.09 Å; As: 1.20 Å) and electronegativity (P: 2.19; As: 2.18).[109] In contrast to phosphorus, antimony, and bismuth, examples of ligand-stabilized polycations of arsenic are rare.

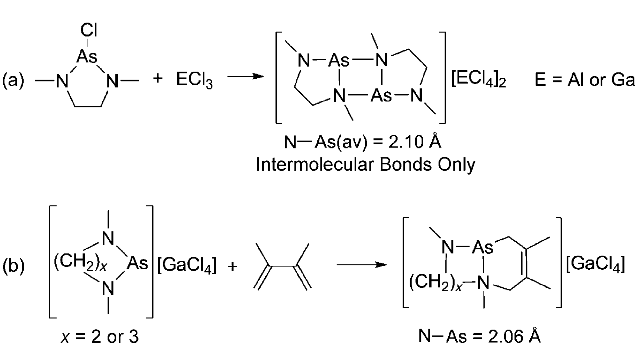
5.1. Nitrogen Donors on Arsenic Acceptors

The earliest inference of a complex which can be interpreted as an amine complex of an arsenium cation was synthesized through displacement of the chloride anion from Ph_2AsCl by NH_2Cl to form $[H_2(Cl)N\text{-}AsPh_2][Cl]$ (Scheme 13), which presumably occurs through an S_N2 mechanism. The products were characterized by elemental analysis and IR spectroscopy, although the latter indicated the presence of some NH_4Cl and $[Ph_2As(Cl)NAs(Cl)Ph_2][Cl]$, the combination of which represent the same empirical formula as the desired product.[63]

$$Ph_2AsCl + H_2NCl \longrightarrow [H_2(Cl)N{-}AsPh_2][Cl]$$

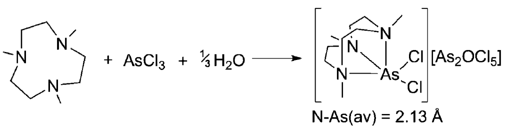
Scheme 13. Synthesis of $[H_2(Cl)N\text{-}AsPh_2][Cl]$.[63]

Donor–acceptor N-As interactions are, however, more convincingly implicated in the solid-state structure of $[(MeN(CH_2)_2NMe)As]_2[ECl_4]_2$ (E = Al or Ga), formed by the reaction of *cyclo*-$(MeN(CH_2)_2NMe)AsCl$ with ECl_3 (Scheme 14).[110] The dimeric structure of the dication contrasts the monomeric structures of *cyclo*-aminophosphenium ions[66] and the alkenic dimerization of isovalent carbenes,[111] germylenes,[112] and stannylenes.[112] The structure also contrasts the monomeric structures observed for related 1,3,2-benzothiazarsolium cations, in which dimerization is precluded by the aromatic character of the bicyclic framework.[113,114] The intermonomer N−As bonds in $[(MeN(CH_2)_2NMe)As]_2[ECl_4]_2$ (2.103(4) Å, $\Sigma_{CR} = 1.91$ Å) are significantly longer than the N−As bonds within the respective five-membered rings (1.752(5) Å and 1.949(4) Å). Intermolecular coordinate bonding is not observed in the analogous six-membered heterocycle, [*cyclo*-$MeN(CH_2)_3NMeAs$][$GaCl_4$], which has been shown to be monomeric in the solid state,[115] but both react with 2,3-dimethyl-1,3-butadiene to give bicylic cationic frameworks (Scheme 14b).[115,116]



Scheme 14. a) Synthesis of $[(MeN(CH_2)_2NMe)As]_2[ECl_4]_2$ (E = Al or Ga)[110] and b) reactions of $[(MeN(CH_2)_xNMe)As]_2[ECl_4]_2$ ($x = 2$ or 3) with 2,3-dimethyl-1,3-butadiene.[115,116]

Two examples of complexes involving multidentate nitrogen ligands on cationic arsenic acceptors have also been reported. The combination of $AsCl_3$ with the tridentate nitrogen donor $Me_3[9]aneN_3$ and a substoichiometric quantity of H_2O furnished $[(Me_3[9]aneN_3)AsCl_2][As_2OCl_5]$ in high yield (Scheme 15).[117] The reaction is envisaged to proceed by the coordination of the nitrogen ligand at the arsenic center effecting halide displacement, with the halide subsequently incorporated into the complex anion. The cation contains a five-coordinate arsenic center, which adopts a distorted square-pyramidal geometry with *cis*-configured nitrogen atoms and the two chloride substituents occupying equatorial sites, and with the N−As bonds comparable with those in the complexes described above.



Scheme 15. Synthesis $[(Me_3[9]aneN_3)AsCl_2][As_2OCl_5]$.[117]

The reaction of $(GuanMes_3)AsCl_2$ with two equivalents of TMSOTf in the presence of 2,2′-bipy (Figure 13a) forms $[(bipy)As(GuanMes_3)][OTf]_2$, which presumably results from the coordination of the neutral bipy ligand to the cationic As center of $[(GuanMes_3)As][OTf]_2$.[118] In the solid state, the cation presents a distorted seesaw geometry, in which the guanidinate ligand interacts asymmetrically with the arsenic center (N-As: 1.872(3) and 2.086(4) Å; $\Sigma_{CR} = 1.91$ Å), as in the neutral precursor, with the bipy ligand interacting similarly, although the differences between the bonds are less pronounced (1.984(5) and 2.141(4) Å; Figure 13b). The asymmetric binding of both ligands, in which the pseudoaxial bonds in both cases are longer than those to pseudoequatorial donors, is consistent with the presence of a stereochemically active lone pair of electrons.

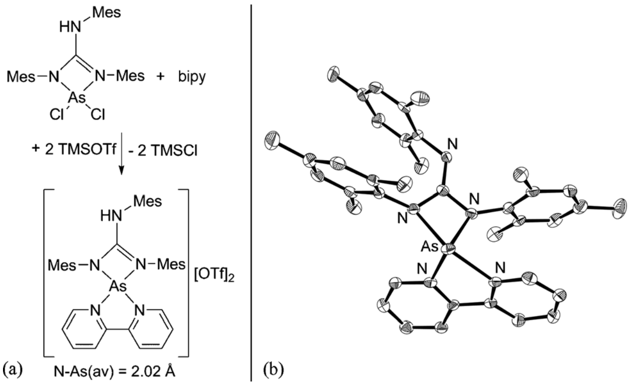
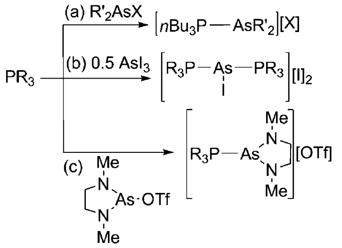


Figure 13. a) Synthesis of $[(bipy)As(GuanMes_3)][OTf]_2$. b) Solid-state structure of the cation.[118]

5.2. Phosphorus Donors on Arsenic Acceptors

Complexes interpreted as phosphine-ligated arsenium cations were first formed by nucleophilic displacement of a halide or the OTf anion from arsines by tertiary alkylphosphines (Scheme 16).[119] The compounds represent some of the earliest Pn–Pn′ complexes that can be envisaged to form through coordination of a pnictine to a pnictenium center and were characterized on the basis of conductivity studies[82] and NMR data.[120]



Scheme 16. Preparation of $[R_3P\text{-}AsR'_2][X]$ and $[(R_3P)_2AsR'][X]_2$ salts by displacement of a halide or trifluoromethanesulfonate from an arsine by an alkylphosphine.

Prototypical, and structurally characterized, intermolecular As-P complexes of the form $[R_3P\text{-}AsR'_2][I]$ were obtained from reactions of tertiary phosphines with iodoarsines, likely proceeding through displacement of an iodide anion through an S_N2 process, with subsequent anion exchange also providing the PF_6 salts (Figure 14a).[33] Both $[Ph_3P\text{-}As(Me)Ph][PF_6]$ (Figure 14b) and $[\{(MeOCH_2)C_6H_4\}Ph_2P\text{-}As(Me)Ph][PF_6]$ were characterized crystallographically as the *R* enantiomers (P-As: 2.3480(6) and 2.3703(4) Å, respectively; $\Sigma_{CR} = 2.29$ Å).

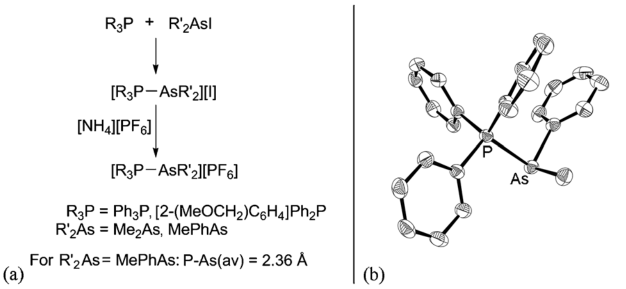


Figure 14. a) Synthesis of $[R_3P\text{-}AsR'_2][X]$. b) Solid-state structure of the cation in $[Ph_3P\text{-}As(Me)Ph][PF_6]$.[33]

Chloride abstraction from heterocyclic chloroarsines with $[K][PF_6]$ in the presence of tertiary phosphines has also been exploited to form enantiomerically pure complexes featuring the $(MeNapth)As^+$ moiety (Figure 15).[121] Similarly, the As-containing heterocycle ANCl activated by TMSOTf or $GaCl_3$ can form monocationic complexes with phosphines or dicationic complexes in the presence of bis(phosphines) (Scheme 17).[122] The seven derivatives that have been characterized crystallographically, for which a representative example is shown in Figure 16a, exhibit a narrow range of P–As bond lengths (2.34–2.42 Å, $\Sigma_{CR} = 2.29$ Å). Shorter bonds are observed in complexes of methylphosphines, presumably a consequence of the increased basicity and reduced steric encumberance of the phosphorus centers. The AN^+ acceptor also forms complexes with *cyclo*-$(CyP)_4$ to yield $[(CyP)_4AN][X]$ (X = OTf or $GaCl_4$), which feature a particularly long P–As bond (2.4660(7) Å, X = OTf; Figure 16b), likely because of the steric strain imposed by the substituents on the tetraphosphine.[31]

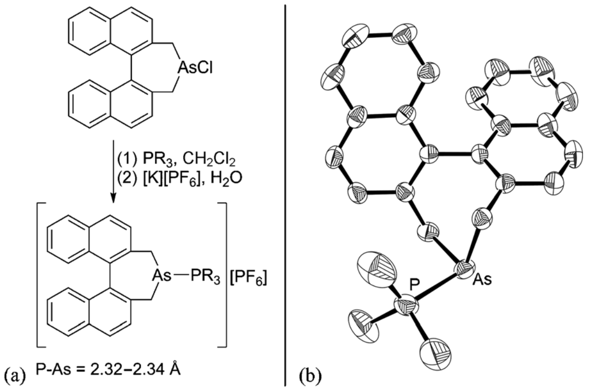
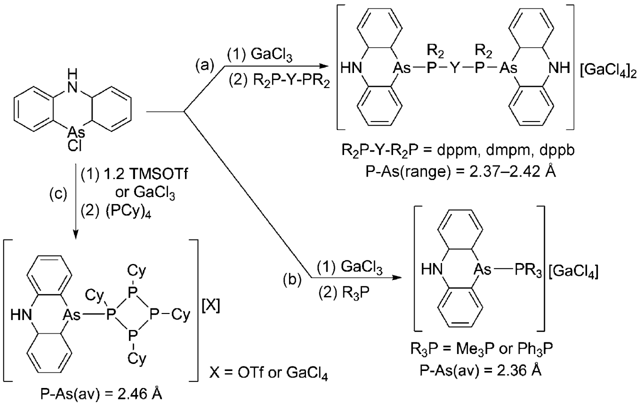


Figure 15. a) Synthesis of $[R_3P\text{-}As(MeNaphth)][PF_6]$ ($R_3P = Me_3P$, Me_2PPh, $Me_2P[C_6H_4(CH_2OMe)]$, or (±)-$[2\text{-}C_6H_4(CH_2OMe)]Me(2\text{-}Naphth)P$. b) Solid-state structure of the cation in $[Me_3P\text{-}As(MeNapth)][PF_6]$.[121]



Scheme 17. Syntheses of phosphine complexes of the $[AN]^+$ acceptor.[122]

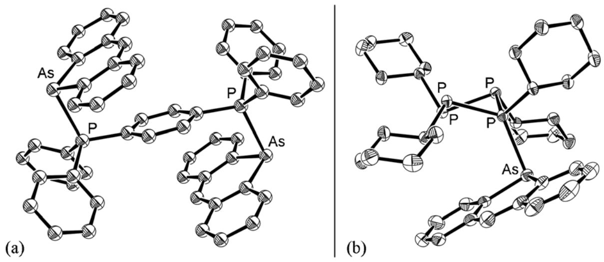


Figure 16. Solid-state structure of a) the dication in $[AN(dppb)AN][GaCl_4]_2$[122] and b) the cation in $[(CyP)_4AN][OTf]$.[31]

Salts that can be interpreted as bis(phosphine) complexes of a diarsenium dication, $[R_3P\text{-}As(Ph)CH_2CH_2(Ph)As\text{-}PR_3]$-

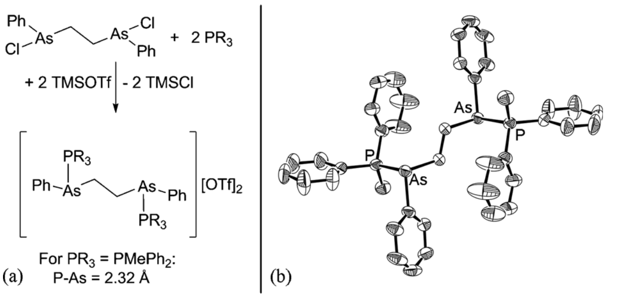
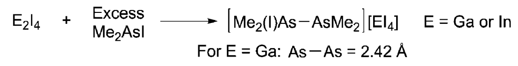


Figure 17. a) Synthesis of $[R_3P\text{-}As(Ph)CH_2CH_2(Ph)As\text{-}PR_3][OTf]_2$ ($R_3P = Me_3P$ or Ph_2MeP). b) Solid-state structure of the cation in the R^*_{As},S^*_{As} diastereomer of $[Ph_2(Me)P\text{-}As(Ph)CH_2CH_2(Ph)As\text{-}P(Me)Ph_2][OTf]_2$.[123]

$[OTf]_2$ ($R_3P = Me_3P$ or $PMePh_2$), can be obtained from chloride abstraction from $Cl(Ph)AsCH_2CH_2As(Ph)Cl$, followed by ligation of the in situ generated diarsenium dication with two phosphine ligands (Figure 17).[123] The bis($PMePh_2$) complex, the only structurally characterized example, displays the expected pyramidal arsenic and tetrahedral phosphorus environments, respectively, with the P–As bond slightly longer than the sum of the covalent radii (2.32 Å, $\Sigma_{CR} = 2.29$ Å). It is also notable that various diastereomers of these compounds are possible, as a result of the presence of stereogenic As centers.

5.3. Arsenic Donors on Arsenic Acceptors

Condensation of Me_2AsI onto solid Ga_2I_4 in vacuo to furnish $[Me_2(I)As\text{-}AsMe_2][GaI_4]$ (Scheme 18) provided the first evidence of a cationic complex that can be envisaged to form through homoatomic As–As coordination chemistry.[124] The compound exhibits a long As–As bond (2.427(5) Å, $\Sigma_{CR} = 2.40$ Å), and the familiar tetrahedral/pyramidal pnictogen centers. Similar structural features were observed for the complexes resulting from reactions of tertiary arsines with Ph(Me)AsCl in the presence of TMSOTf (Figure 18a).[125] In cases where the substituents at the tertiary As center contains pendant O donors, a coordinate interaction is observed between the acceptor arsenic center and pendant O substituent (Figure 18b).



Scheme 18. Syntheses of $[Me_2(I)As\text{-}AsMe_2][EI_4]$ (E = Ga or In).[124]

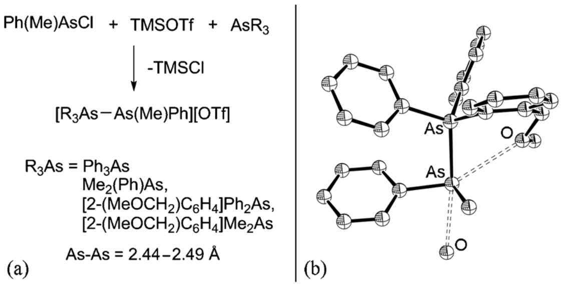


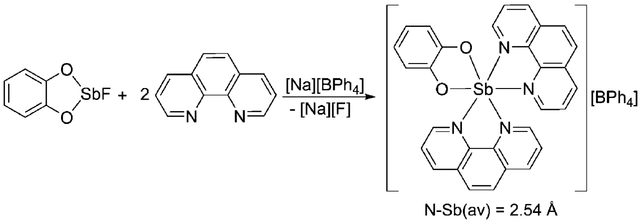
Figure 18. a) Synthesis of $[R_3As\text{-}As(Me)Ph][OTf]$. b) Solid-state structure of $[(\{2\text{-}MeOCH_2\}Ph)Ph_2As\text{-}AsMePh][OTf]$. For clarity, only the coordinating O atom of the triflate anion is shown.[125]

6. Cationic Complexes of Antimony Acceptors

Compounds of the heavier p-block elements generally exhibit greater Lewis acidity than their lighter congeners, and in this context, an array of coordination complexes has been reported for neutral Sb^{III} and Sb^{V} acceptors.[1,2] However, the introduction of a positive charge at antimony through ligand displacement/abstraction both enhances the Lewis acidity and creates a vacant site for coordination of a donor. A diverse series of salts have been reported that are interpreted as mono-, di-, and tricationic antimony acceptors ligated by one or more pnictine donors.

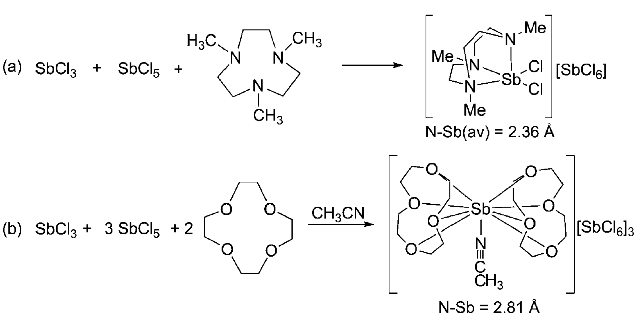
6.1. Nitrogen Donors on Antimony Acceptors

A variety of complexes can be interpreted as stibenium cations (class **2A** acceptors) ligated by intramolecular nitrogen donors, and this class of compounds, along with analogous neutral compounds, has been the subject of a recent review.[126] Intermolecular N-Sb coordinate bonding can also be invoked in the synthesis of structurally distinct cations, including the catecholatostibenium cation, $[C_6H_4O_2Sb]^+$, formed through treatment of $C_6H_4O_2SbF$ with [Na][BPh_4] in the presence of two equivalents of phenanthroline (phen; Scheme 19).[127] In the solid state, the cation adopts a VSEPR-consistent distorted pentagonal pyramidal geometry at the Sb center, with long N–Sb bonds (average 2.54 Å, $\Sigma_{CR} = 2.11$ Å), consistent with those observed for related neutral compounds containing coordinate N–Sb bonds.[128,129]



Scheme 19. Synthesis of $[(phen)_2Sb(O_2C_6H_4)][BPh_4]$.[127]

Multidentate ligands have also been demonstrated to form isolable complexes with stibenium centers, the earliest such example, $[(Me_3[9]aneN_3)SbCl_2][SbCl_6]$, resulted from the reaction of $SbCl_3$ with $SbCl_5$ in the presence of the azacycle $Me_3[9]aneN_3$ (Scheme 20a).[130] The cation exhibits a square-pyramidal environment at Sb, with a facial configuration of the nitrogen donor centers enforced by the lone pair of electrons at the Sb center. The N–Sb bonds range from 2.313(7) to 2.400(7) Å ($\Sigma_{CR} = 2.11$ Å), with the shortest



Scheme 20. Synthesis of a) $[(Me_3[9]aneN_3)SbCl_2][SbCl_6]$[130] and b) $[(CH_3CN)Sb([12]crown\text{-}4)_2][SbCl_6]_3$.[131]

interaction evidenced for the nitrogen center *trans* to the lone pair of electrons.

The related reaction of $SbCl_3$ with $SbCl_5$ and [12]crown-4 in acetonitrile gives $[(CH_3CN)Sb([12]crown\text{-}4)_2][SbCl_6]_3$, which is described as a complex of Sb^{3+} (class **2C** acceptor) ligated by two crown ether ligands and a molecule of CH_3CN (Scheme 20b).[131] The antimony center is coordinated by eight oxygen atoms in a sandwich-like structure, with the nitrogen center of acetonitrile inserted between the ether rings and a long Sb–N bond (2.810(9) Å, $\Sigma_{CR} = 2.11$ Å). Nevertheless, the N–Sb bond is slightly shorter than those reported for other cationic complexes containing $CH_3CN\text{-}Sb^+$ interactions, namely the monocationic $[(CH_3CN)Sb_2Cl_5(NPMe_3)_2][SbCl_6]$ (3.010(4) Å) and dicationic $[(CH_3CN)_2SbCl(NPPh_3)]_2[SbCl_6]_2$ (average: 2.874(4) Å),[132] which reflects the greater positive charge at the antimony center in the tricationic complex.

Related complexes of cationic antimony centers with chelating donors have also been reported. For example, a series of 2,2′-bipy ligated cations was formed by exploiting the sequential abstraction of fluoride anions from SbF_3, through stoichiometric combination with TMSOTf and bipy (Figure 19a).[23] The solid-state structure of $[(bipy)SbF_2][OTf]$ confirms the presence of one chelate ligand bound to an SbF_2^+ acceptor (Figure 19b), while the structure of $[(bipy)_2Sb][OTf]_3$ contains an Sb^{3+} center ligated by two chelate ligands (Figure 19c). NBO analysis of $[(bipy)_2Sb]^{3+}$ indicates a residual charge of +1.77 e at antimony, thus suggesting a high Lewis acidity. In addition, the optimized structure of the hypothetical $[(bipy)_3Sb]^{3+}$ is calculated to be 250 kJ mol^{-1} lower in energy than that determined for $[(bipy)_2Sb]^{3+}$ and free bipy. Nevertheless, $[(bipy)_3Sb]^{3+}$, a main-group analogue of the archetypal transition-metal coordination complex $[Ru(bipy)_3]^{2+}$,[133] has yet to be realized experimentally, perhaps because of the presence of the stereochemically active lone pair of electrons at antimony.

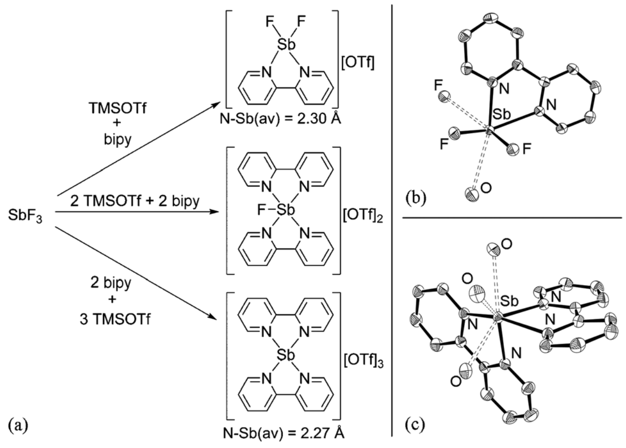


Figure 19. a) Synthesis of 2,2′-bipy complexes of $[SbF_{3-x}]^{x+}$ and solid-state structure of the cations in b) $[(bipy)SbF_2][OTf]$ and c) $[(bipy)_2Sb][OTf]_3$.[23] In (b) and (c), the oxygen and fluorine atoms of the triflate anions involved in interion contacts are shown.

In addition to complexes of electron-rich (lone pair bearing) antimony centers, preliminary reports have appeared of amine-stabilized complexes of R_3Sb^{2+}, $[R_3Sb(L\text{-}L)]^{2+}$ (R = alkyl or aryl; L = 2,2-bipy or 1,2-diaminoethane),[134] and R_2Sb^{3+} (R = aryl; L = pyridine-*N*-oxide or α/β/γ-picoline),[135] which represent rare examples of class **3B** and **3C** acceptors, respectively. These complexes are reported to result from halide abstraction from R_3SbCl_2 or R_2SbCl_3 in the presence of the donor ligand, and have been characterized by IR and ^{1}H NMR spectroscopy, elemental analysis, and conductivity studies.[135b]

6.2. Phosphorus Donors on Antimony Acceptors

A diverse array of cations containing P–Sb bonds have been obtained by halide abstraction from SbX_3 and Ph_2SbX in the presence of phosphine or diphosphine donors. The first examples were formed by reaction of Ph_2SbX (X = Cl or Br) and PMe_3 with a substoichiometric quantity of $[NH_4][PF_6]$ (Figure 20a), and were found in the solid state to consist of four $[Me_3P\text{-}SbPh_2]^+$ moieties around a halide core, with the formula $[(Me_3P\text{-}SbPh_2)_4X][PF_6]_3$ (X = Cl or Br; Figure 20b).[136] A prototypical monomeric analogue, $[Ph_3P\text{-}SbPh_2][PF_6]$, was subsequently obtained from the reaction of Ph_2SbCl and $[Tl][PF_6]$ in a 1:1 ratio in the presence of PPh_3 (Figure 21a),[21] and exhibits a P–Sb bond length (2.5950(12) Å, $\Sigma_{CR} = 2.49$ Å) that is essentially identical to that observed in $[(Me_3P\text{-}SbPh_2)_4X][PF_6]_3$. In the presence of excess PPh_3, a *trans*-configured bis(phosphine) derivative, $[(Ph_3P)_2SbPh_2][PF_6]$, is obtained (Figure 21b,c), which exhib-

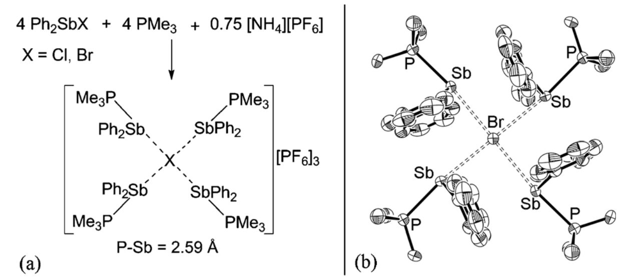


Figure 20. a) Synthesis of $[(Me_3P\text{-}SbPh_2)_4X][PF_6]$ (X = Cl or Br). b) Solid-state structure of the trication with X = Br.[136]

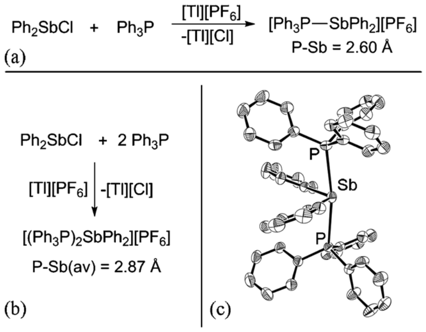


Figure 21. Synthesis of a) [Ph_3P-$SbPh_2$][PF_6] and b) [$(Ph_3P)_2SbPh_2$][PF_6]. c) Solid-state structure of the cation in (b).[21]

its a mean Sb–P bond length (2.8683(9) Å) that is significantly longer than in [Ph_3P-$SbPh_2$][PF_6].

The diphosphines dmpe, dppe, dmpm, and dppm have also been shown to form chelate complexes with stibenium cations (class **2A** acceptors) and stibinidinium dications (class **2B** acceptors).[137] Mixtures of $SbCl_3$, $AlCl_3$, and the chelating phosphines dppm, dmpm, dppe, and dmpe (Figure 22 a) led to monocationic cyclic structures, generally involving symmetric binding of the diphosphine to the Sb center, with the P–Sb bond lengths of 2.5–2.6 Å consistent with P–Sb bonds in related compounds.[21,136,138] The presence of excess $AlCl_3$ effects abstraction of two chloride anions and formation of complexes of the form [$(R_2P(CH_2)_xPR_2)SbCl$][$AlCl_4$]$_2$, with the solid-state structures of [(dppe)SbCl][$AlCl_4$]$_2$ (Figure 22 b) and [(dppm)SbCl][$AlCl_4$]$_2$ elucidated. In both cases, symmetric binding of the chelating phosphine is seen, with the P–Sb bond lengths similar in magnitude to those of the monocations. The latter complexes may be described as $ClSb^{2+}$ acceptors (class **2B**) stabilized by the interaction of the two phosphorus donors of a chelating diphosphine.

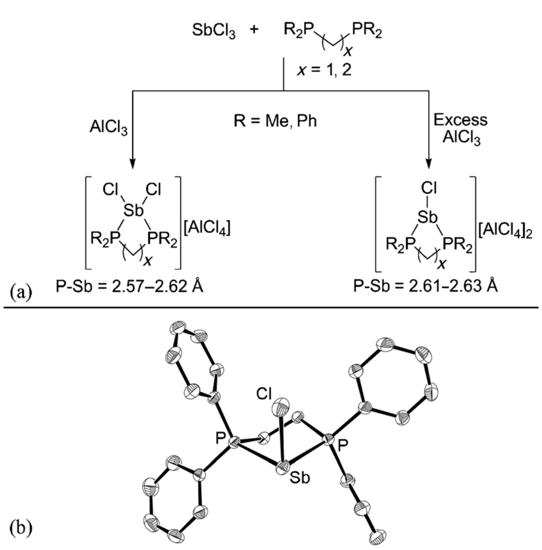


Figure 22. a) Synthesis of complexes of $SbCl_2^+$ and $SbCl^{2+}$ with chelating diphosphines. b) Solid-state structure of the dication in [(dppe)SbCl][$AlCl_4$]$_2$.[137]

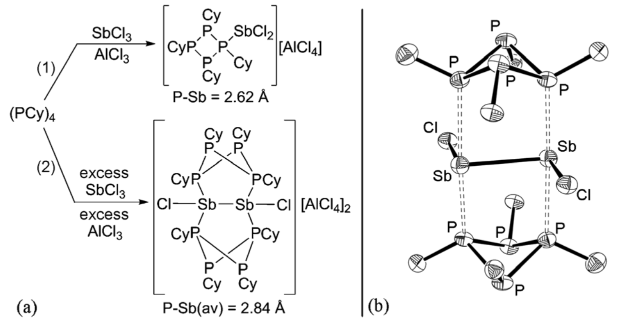


Figure 23. a) Synthesis of [$(PCy)_4SbCl_2$][$AlCl_4$] and [$\{(CyP)_4\}_2Sb_2Cl_2$][$AlCl_4$]$_2$. b) Solid-state structure of the cation in [$\{(CyP)_4\}_2Sb_2Cl_2$][$AlCl_4$]$_2$. For clarity only the *ipso*-carbon atoms of cyclohexyl groups are shown.[31]

The corresponding reaction of $SbCl_3$ and $AlCl_3$ in the presence of *cyclo*-$(PCy)_4$ furnishes a P–Sb bond through interaction of the *cyclo*-phosphine with a Cl_2Sb^+ moiety (Figure 23 a, reaction 1).[31] However, in the presence of excess $AlCl_3$ and $SbCl_3$, a complex presented as a bis(tetraphosphine)-stabilized dichlorodistibenium dication was isolated (Figure 23 a, reaction 2). The solid-state structure of this compound indicates a centrosymmetric cationic unit containing a ClSb-SbCl core, in which the two Sb centers are doubly bridged by chelating $(PCy)_4$ moieties (Figure 23 b). The Sb centers of the planar ClSb-SbCl unit are in a see-saw geometry, with the phosphorus centers in highly distorted tetrahedral environments as a result of the constraints of the phosphorus cycle. The P–Sb bonds average 2.84 Å, which corresponds to a significant elongation from that present in [$(CyP)_4SbCl_2$][$AlCl_4$] (2.6177(7) Å, $\Sigma_{CR} = 2.49$ Å). The [ClSb-SbCl]$^{2+}$ dicationic core of the complex is perceived to result from a redox reaction, possibly by disproportionation of $SbCl_3$ to form $SbCl_5$ and Sb_2Cl_4, with chloride abstraction.

Redox processes at Sb were also demonstrated in the synthesis of the unusual tetraphosphorus-tetraantimony salt, [$(Me_3P$-$Sb)_4$][OTf]$_4$,[24] which was synthesized in high yield by reaction of SbF_3 with TMSOTf and PMe_3 in a 1:3:3 ratio (Figure 24 a), or reaction of [$(bipy)_2Sb$][OTf]$_3$[23] with PMe_3 in a 1:3 ratio. The solid-state structure of the cation comprises a folded Sb_4 ring with a single PMe_3 moiety bound to each Sb

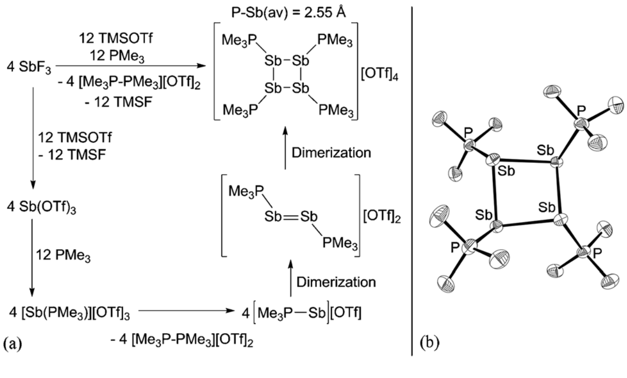


Figure 24. a) Synthesis and proposed mechanism for the formation of [$(Me_3P$-$Sb)_4$][OTf]$_4$. b) Solid-state structure of the cation.[24]

center (Figure 24 b) and four essentially identical P–Sb bonds (average 2.554(2) Å, $\Sigma_{CR} = 2.49$ Å) of similar magnitude to P–Sb bonds in other cationic complexes.[21,136,137] The Sb–Sb bonds (average 2.8490(6) Å) are comparable with those in the isoelectronic neutral cyclotetrastibine $(t\mathrm{BuSb})_4$ and in other cationic complexes containing Sb–Sb bonds (see Section 6.4).[139–141] Mechanistic insight into the formation of this product was attained by monitoring the reaction at low temperature using ^{31}P NMR spectroscopy, which revealed the formation of $[(Me_3P)_3Sb][OTf]_3$, a tris(phosphine) complex of Sb^{3+} (class **2C**), as a key intermediate. Reductive elimination of $[Me_3P\text{-}PMe_3][OTf]_2$ from this species is speculated to form $[Me_3P\text{-}Sb][OTf]$, which is postulated to then undergo a double dimerization to yield the tetramer (Figure 24 a). Computational analysis of the cation indicates significant delocalization of the charge onto the phosphine ligands, with a net charge of only $+0.81\,e$ remaining on the Sb_4 unit. In this respect, the complex may be described as *cyclo*-tetrastibinotetraphosphonium salt.

6.3. Arsenic Donors on Antimony Acceptors

The only examples of cations containing As–Sb bonds result from the reaction of $SbCl_3$, TMSOTf, and $AsMe_3$ to form $[Me_3As\text{-}SbCl_2][OTf]$, and from the reaction of $PhSbCl_2$, $AlCl_3$, and $AsPh_3$ to form $[Ph_3As\text{-}Sb(Cl)Ph][AlCl_4]$ (Figure 25).[142] Analogous in structure to the corresponding complexes with phosphine donors, $[R_3P\text{-}SbR'_2][X]$, these compounds are exemplified by $[Me_3As\text{-}SbCl_2][OTf]$, which exhibits an As–Sb bond (2.6676(4) Å, $\Sigma_{CR} = 2.60$ Å) that is slightly shorter than that in $[Ph^3As\text{-}Sb(Cl)Ph][AlCl_4]$ (2.6991(3) Å; Figure 25 b) and the neutral adduct $Et_3As\text{-}SbCl_3$ (2.6803(10) Å).[142]

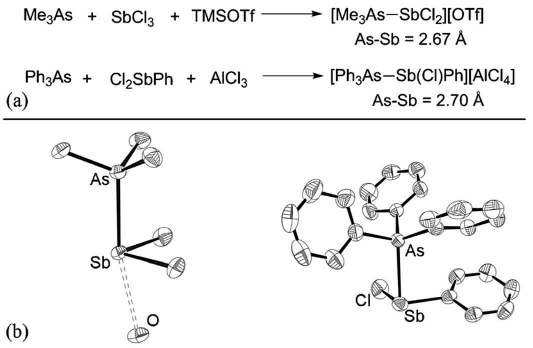


Figure 25. a) Syntheses of $[R_3As\text{-}Sb(Cl)R'][X]$ salts. b) Solid-state structures of the cations in $[Me_3As\text{-}SbCl_2][OTf]$ and $[Ph_3As\text{-}Sb(Cl)Ph][AlCl_4]$.[142]

6.4. Antimony Donors on Antimony Acceptors

Catena-antimony cations with two and three antimony centers represent heavier analogues of the *catena*-phosphorus cations described earlier. The prototypical complex of a stibine ligand on a stibenium center was isolated as $[Me_3Sb\text{-}SbMe_2]_2[Me_3SbBr_3]_2$ (Sb-Sb: 2.821(1) Å, $\Sigma_{CR} = 2.80$ Å) in 80% yield from molten Me_2SbBr, which is postulated to disproportionate to Me_3Sb and $MeSbBr_2$ and engage in equilibria with the starting material to furnish the observed product[140] through a coordinate interaction of Me_3Sb with Me_2SbBr (Figure 26).

Me_2SbBr also reacts with $Me_2Sb\text{-}SbMe_2$ as both an abstracting agent and a source of Me_2Sb^+ (Figure 27 a) to give $[Me_2Sb\text{-}Sb(Me)_2\text{-}SbMe_2][Me_2SbBr_2]$ (Figure 27 b),[139] which contains a cation that is analogous to $[Me_2P\text{-}P(Me)_2\text{-}PMe_2]^+$ (see Section 4.2).[100] The triantimony salt can be considered as a complex of a distibine ligand on a stibenium cation, although in the solid state the cation is symmetric, consistent with a distibinostibonium formulation, and the Sb–Sb bonds (2.8203(5) Å, $\Sigma_{CR} = 2.80$ Å) are almost identical to that of $[Me_3Sb\text{-}SbMe_2]^+$. The salt was found to be unstable in solution, decomposing to its initial constituents, $Me_2Sb\text{-}SbMe_2$ and Me_2SbBr.

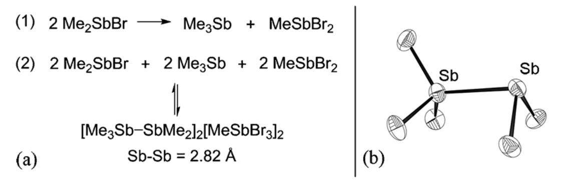


Figure 26. Synthesis and proposed mechanism for the formation of $[Me_3Sb\text{-}SbMe_2]_2[Me_3SbBr_3]_2$. b) Solid-state structure of the cation.[140]

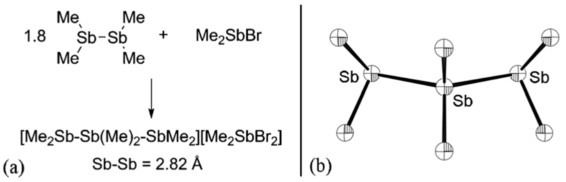


Figure 27. a) Synthesis of $[Me_2Sb\text{-}Sb(Me)_2\text{-}SbMe_2][Me_2SbBr_2]$. b) Solid-state structure of the cation.[139]

Small quantities of $[(Me_3Sb)_2SbMe][GaCl_4]_2$, which can be interpreted as a bis(stibine) complex of $MeSb^{2+}$, have been isolated along with $[Me_3Sb\text{-}SbMe_2][GaCl_4]$ from the reaction of $(Me_3Si)_2N\text{-}SbCl_2$ with $GaCl_3$ at low temperature (Figure 28 a).[141] The salt contains two distinct formula units in the asymmetric unit, with an average Sb–Sb bond length of 2.822(1) Å ($\Sigma_{CR} = 2.\ 80$ Å; Figure 28 b), which is similar to

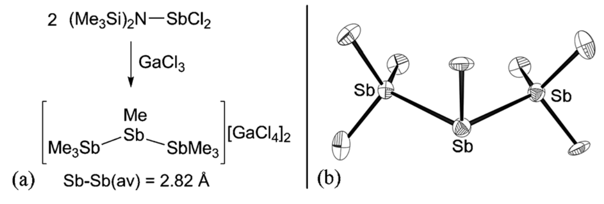


Figure 28. a) Synthesis of $[(Me_3Sb)_2SbMe][GaCl_4]_2$. b) Solid-state structure of the cation.[141]

those observed in $[Me_3Sb\text{-}SbMe_2]^+$ and $[Me_2Sb\text{-}Sb(Me)_2\text{-}SbMe_2]^+$, despite the greater positive charge on the cation in this case.[139,140]

7. Cationic Complexes of Bismuth Acceptors

Despite the high Lewis acidity and metallic character of bismuth, complexes of pnictine ligands with cationic bismuth centers are the least developed of the interpnictogen cations. By comparison, there are many reports of the synthesis and comprehensive characterization of bismuthenium cations stabilized by Group 16 donors, such as $OPPh_3$,[143] $OP(NMe_2)_3$,[143–146] crown ethers,[147,148] and $OAsPh_3$,[149] which suggests that future research may yield an increased library of pncitine-ligated bismuth cations. Nonetheless, complexes of R_2Bi^+, RBi^{2+}, and Bi^{3+} (classes **2A**, **2B**, and **2C** acceptors, respectively) with donors based on nitrogen, phosphorus, arsenic, and antimony have been reported. Additionally, bismuth has a much larger coordination sphere compared to the rest of the pnictogen elements and it is not unusual for bismuth to interact with several multidentate ligands, atypical of the other pnictogen elements.

7.1. Nitrogen Donors on Bismuth Acceptors

Neutral complexes of bismuth with intramolecular nitrogen donors are well-established, but of those with halide functionality, few lead to additional N-Bi interactions upon halide abstraction. Treatment of $[(2\text{-}\{Me_2NCH_2\}C_6H_4)_2BiCl]$ with $[Tl][PF_6]$, however, furnishes a bismuth cation in which the Bi center interacts with both pendant nitrogen donors, in contrast to only one in the neutral precursor (see Figure 29).[138] The N–Bi bond lengths in the cation (average: 2.50 Å, $\Sigma_{CR} = 2.21$ Å) are slightly shorter than those observed in the neutral species [Bi-N: 2.570(5) Å], thus implicating a greater Lewis acidity for the Bi center, in line with the interpretation of this species as a ligand-stabilized bismuthenium complex.

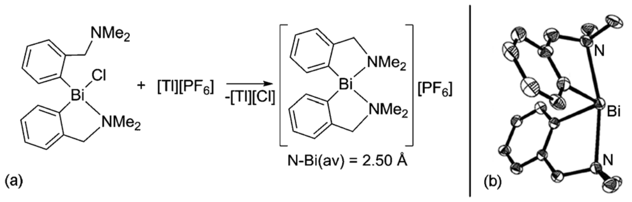
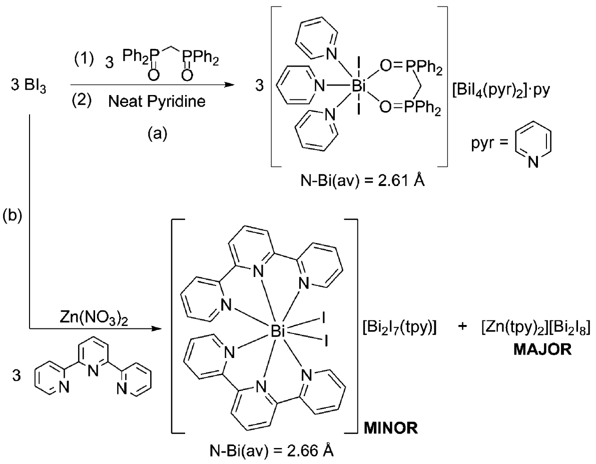


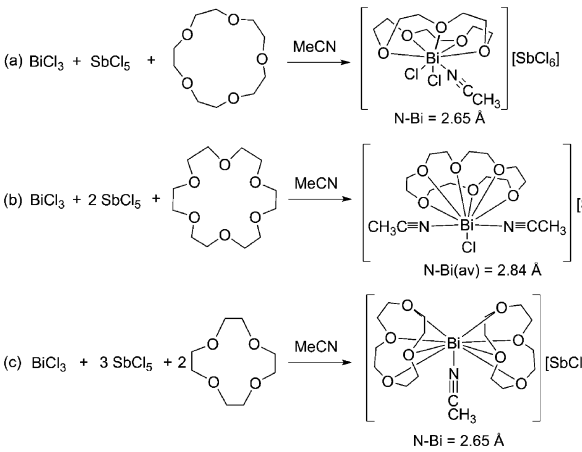
Figure 29. a) Synthesis of $[(2\text{-}\{Me_2NCH_2\}C_6H_4)_2Bi][PF_6]$. b) Solid-state structure of the cation.[138]

Examples of complexes resulting from the intermolecular donor–acceptor interactions between nitrogen donor ligands and bismuthenium cations (class **2A** acceptors) have also been reported, with the most abundant subclass being that of BiX_2^+ (X = halide) acceptors. An early example of these complexes, a tris(pyridine) complex of BiI_2^+, was obtained following recrystallization of the neutral adduct $(dppom)BiI_3$ from pyridine. This process leads initially to halide displacement at bismuth, eventually yielding $[BiI_2(pyr)_3(dppom)][BiI_4(pyr)_2]\cdot pyr$ (Scheme 21 a).[143] The multidentate nitrogen donor tpy also provides stabilization of BiI_2^+ in $[BiI_2(tpy)_2][Bi_2I_7(tpy)]$, which is formed in low yield in the solvothermal reaction of BiI_3 and $Zn(NO_3)_2\cdot 6H_2O$ in the presence of tpy (Scheme 21 b).[150] In this case, the N–Bi bond lengths vary from 2.544(9) Å to 2.787(10) Å ($\Sigma_{CR} = 2.21$ Å).



Scheme 21. Synthesis of a) $[BiI_2(pyr)_3(dppom)][BiI_4(pyr)_2]\cdot pyr$[143] and b) $[BiI_2(tpy)_2]\,[Bi_2I_7(tpy)]$.[150]

As demonstrated for antimony, a series of crown ether/acetonitrile complexes of $BiCl_2^+$, $BiCl^{2+}$, and Bi^{3+} (class **2A**, **2B**, and **2C** acceptors, respectively) was obtained through chloride abstraction from $BiCl_3$ by $SbCl_5$ in the presence of various crown ethers in CH_3CN solution (Scheme 22).[131,151]



Scheme 22. Synthesis of mono-, di-, and trications of Bi, stabilized by crown ether and acetonitrile donors.[131,151]

The monocation interacts with one crown ether and one molecule of CH_3CN, the dication with one crown ether and two molecules of CH_3CN, and the trication with two crown ether molecules, which sandwich the bismuth center, and one molecule of CH_3CN, analogous to the structure of $[(CH_3CN)Sb([12]crown\text{-}4)_2][SbCl_6]_3$ (Section 6.1). In each case, the bismuth center engages all oxygen centers of the crown ether molecules and exhibits a range of N-Bi distances averaging 2.65(3) Å, 2.84(3) Å, 2.650(9) Å, for the mono-, di-, and trications, respectively ($\Sigma_{CR} = 2.21$ Å).

7.2. Phosphine Donors on Bismuth Acceptors

The only examples of cations involving P−Bi bond(s), $[Ph_3P\text{-}BiPh_2][PF_6]$ and $[(Ph_3P)_2BiPh_2][PF_6]$, are formed in the reaction of Ph_2BiCl, $[Tl][PF_6]$, and one or two equivalents of PPh_3 (Figure 30 a).[21] The bis(phosphine) adduct, $[(Ph_3P)_2BiPh_2][PF_6]$, (Figure 30 b) reveals a seesaw geometry at the bismuth center, analogous to that in the antimony derivative[21] (see Section 6.2), with the PPh_3 moieties occupying axial positions and imposing long Bi−P bonds (average: 2.952(9) Å, $\Sigma_{CR} = 2.59$ Å).

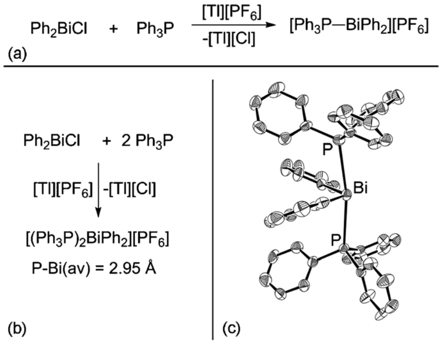


Figure 30. Synthesis of a) $[Ph_3P\text{-}BiPh_2][PF_6]$ and b) $[(Ph_3P)_2BiPh_2][PF_6]$. c) Solid-state structure of the cation in (b).[21]

7.3. Arsenic Donors on Bismuth Acceptors

The reaction of $BiCl_3$ with TMSOTf in the presence of $AsPh_3$ provides a route to complexes of the form $[(Ph_3As)_xBiCl_2][OTf]$ (Figure 31)[142,152] through halide abstraction. The structures are analogous to those of the phosphine complexes, with the bis(arsine) complex (Figure 31 b) exhibiting longer As−Bi bonds (average: 3.02 Å, $\Sigma_{CR} = 2.70$ Å) than the mono(arsine) species (2.88 Å), likely as a result of the quenching of the Lewis acidity at Bi associated with the coordination of the first arsine ligand, and to the *trans* configuration of the ligands.

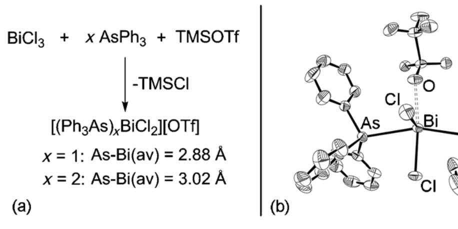


Figure 31. a) Synthesis of $[(Ph_3As)_xBiCl_2][OTf]$ ($x = 1$ or 2) salts. b) Solid-state structure of $[(Ph_3As)_2BiCl_2][OTf]$.[142]

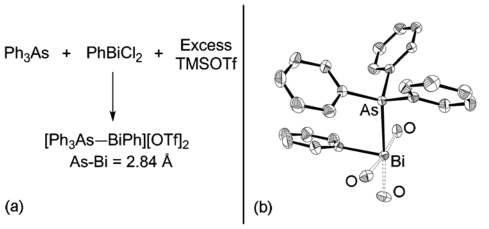


Figure 32. a) Synthesis of $[Ph_3As\text{-}BiPh][OTf]_2$. b) Solid-state structure of the cation showing oxygen atoms with interion contacts to three triflate anions.[152]

The reaction of $PhBiCl_2$ and $AsPh_3$ in the presence of excess TMSOTf yields the mono(arsine) complex $[Ph_3As\text{-}BiPh][OTf]_2$ (Figure 32),[152] in which the As−Bi bond (2.84 Å) is slightly shorter than that in $[Ph_3As\text{-}BiCl_2][OTf]$.[142] The relatively small contraction in bond length, despite the dicationic nature of the Bi center, can be attributed to the interaction of the Bi center with oxygen atoms of three triflate anions, which reduces the effective Lewis acidity. Together with the stibine complex, $[Ph_3Sb\text{-}BiCl][AlCl_4]_2$ (see Section 7.4), these compounds represent the first pnictine-stabilized Bi dications, and are examples of carbenoid (6-valence) Bi centers (class **2B** acceptors).

7.4. Antimony Donors on Bismuth Acceptors

The stibine complexes of $BiCl_2^+$ and $BiCl^{2+}$ in $[Ph_3Sb\text{-}BiCl_2][AlCl_4]$ and $[Ph_3Sb\text{-}BiCl][AlCl_4]_2$ are, to our knowledge, the only examples of compounds containing $Sb\text{−}Bi^+$ bonds. They represent analogues of the previously described arsine complexes and were obtained by using the same procedures (Figure 33 a).[152] In both cases, the solid-state structures indicate that the bismuth center engages in an η^6-interaction with an arene solvent molecule, as well as two $AlCl_4$ anions, with Sb−Bi bond lengths of 3.0199(4) and 2.9707(3) Å ($\Sigma_{CR} = 2.90$ Å) for the complexes of $BiCl_2^+$ and $BiCl^{2+}$, respectively. The dicationic salt, $[Ph_3Sb\text{-}BiCl][AlCl_4]_2$, demonstrates a distorted pentagonal-bipyramidal geometry at bismuth, in which an η^6-bound benzene molecule occupies an axial site *trans* to the stibine donor (Figure 33 b). The monocation adopts a similar conformation, based on a distorted octahedron, with two Bi-Cl contacts to the anion.

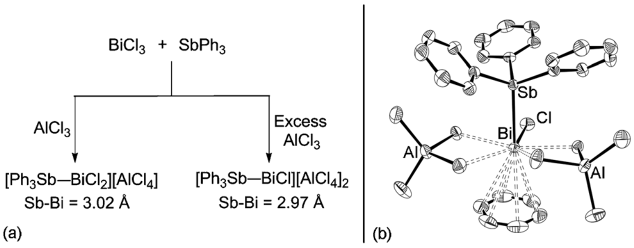


Figure 33. a) Synthesis of $[Ph_3Sb\text{-}BiCl_2][AlCl_4]$ and $[Ph_3Sb\text{-}BiCl][AlCl_4]_2$. b) Solid-state structure of $[Ph_3Sb\text{-}BiCl][AlCl_4]_2$.[152]

8. Summary and Outlook

Examples of cations resulting from interpnictogen donor–acceptor interactions have been known for more than 50 years, but recent reports of structural confirmation and extensive diversification of these complexes have established a new direction in coordination chemistry. Examples of complexes derived from homoatomic P-P interactions are most well developed, and offer a versatile synthetic approach to polyphosphorus frameworks that prompt comparison with the diagonally related hydrocarbons. The halide-abstraction/donor coordination synthetic method is generally applicable as a rapid and facile means of forming Pn−Pn and Pn′−Pn bonds. The commercial availability of many abstracting agents and ligands bodes well for the discovery and development of these element–element bond forming reactions, and Table 2 provides an overview of Pn−Pn and Pn′−Pn bonds that have been structurally characterized in cationic frameworks.

Table 2: Structurally characterized (●) Pn−Pn and Pn′−Pn bonding motifs in cationic frameworks.

Donor	Acceptor				
	N	P	As	Sb	Bi
N	●	●	●	●	●
P	●	●	●	●	●
As	●	●	●	●	●
Sb	–	●	–	●	●
Bi	–	–	–	–	–

While most of the compounds reported are formed from the interaction of pnictogen acceptors with amine, phosphine, or arsine donors, recent discoveries of stibine donors on phosphorus, antimony, and bismuth acceptors prompts a more comprehensive development of complexes between the heavier pnictogens. In this context, there are currently no examples of compounds formed from the interaction of bismuth donors with pnictogen acceptors, thereby highlighting the relatively low Lewis basicity of bismuthines. Nevertheless, we envisage that appropriate substitution at bismuth (e.g. with electron-donating groups) and at the pnictogen acceptor centers (e.g. with electron-withdrawing groups), together with the introduction of a greater cationic charge will enable Bi-Pn donor–acceptor interactions.

Despite the now extensive library of interpnictogen cations, the reactivity and properties of these compounds has yet to be significantly explored. We anticipate that the fundamental development of coordination chemistry between the pnictogens, and the p-block elements in general, will lead to the discovery of new materials and catalysts to rival those developed from the chemistry of carbon and transition metals.

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[11] ANCl = 10-chloro-5-hydrophenarsazine; bipy = 2,2′-bipyridine; dbn = 1,5-diazabicyclo[4.3.0]non-5-ene; DFT = density functional theory; dmap = 4-(dimethylamino)pyridine; dppe = 1,2-bis(diphenylphosphino)ethane; dppm = bis(diphenylphosphino)methane; dmpe = 1,2-bis(dimethylphosphino)ethane; dmpm = bis(dimethylphosphino)methane; dppom = $Ph_2(O)PCH_2P(O)Ph_2$; GuanMes$_3$ = *N,N′,N″*-tris(2,4,6-trimethylphenyl)guanidinate, Me$_3$[9]aneN$_3$ = 1,4,7-trimethyl-1,4,7-triazacyclononane; MeNapth = 2,2′-bis(methylene)-1,1′-binaphthylyl; Mes = 2,4,6-trimethylphenyl; Mes* = 2,4,6-tri-*tert*-butylphenyl; N-bian = pyridyl-tethered 1,2-bis(imino)acenaphthene; phen = phenanthroline; pyr = pyridine; pyra = 3,5-dimethylpyrazole; quin = quinuclidine; OTf = trifluoromethanesulfonate; tmeda = *N,N,N′,N′*-tetramethylethylenediamine; TMS = trimethylsilyl; tpy = 2,2′:6′2″-terpyridine; triam = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine; Σ_{CR} = sum of the covalent radii of two feature elements.
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